

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE 27 Dec 95	3. REPORT TYPE AND DATES COVERED
----------------------------------	-----------------------------	----------------------------------

4. TITLE AND SUBTITLE Water Washing of Polycyclic Aromatic Hydrocarbons from Soils.	5. FUNDING NUMBERS
---	--------------------

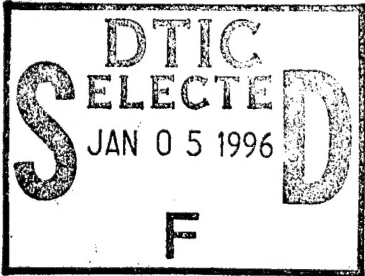
6. AUTHOR(S) Paula Anne Tholson	
------------------------------------	--

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) AFIT Students Attending: Minnesota University	8. PERFORMING ORGANIZATION REPORT NUMBER 95-143
--	---

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) DEPARTMENT OF THE AIR FORCE AFIT/CI 2950 P STREET, BLDG 125 WRIGHT-PATTERSON AFB OH 45433-7765	10. SPONSORING/MONITORING AGENCY REPORT NUMBER
--	---

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT Approved for Public Release IAW AFR 190-1 Distribution Unlimited BRIAN D. Gauthier, MSgt, USAF Chief Administration	12b. DISTRIBUTION CODE
--	------------------------

13. ABSTRACT (Maximum 200 words) 

19960104 148

14. SUBJECT TERMS			15. NUMBER OF PAGES 84
			16. PRICE CODE
17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT

Author: Paula Anne Thorson

Title: Water Washing of Polycyclic Aromatic Hydrocarbons from Soils

Rank: 2Lt

Service Branch: Air Force

Date: 1995

Number of Pages: 84

Degree awarded: M.S. in Civil Engineering

Institution: University of Minnesota

Accession For	
NTIS CRA&I	<input checked="checked" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By	
Distribution /	
Availability Codes	
Dist	Avail and/or Special
A-1	

ABSTRACT

Dissolution studies were carried out using batch operations with Jordan sand. The low organic content sand was coated with varying concentrations of phenanthrene and pyrene. Hexane was used to dissolve the chemicals and then coat the sand. Double distilled water was used to wash the various coated sands. The water was analyzed and replaced with new water every four days.

Lower solubilities were obtained for phenanthrene at lower soil concentrations. Strong linear correlations were observed over short ranges of about 0.1 mg/g or less. However there was evidence that a nonlinear function would be necessary to describe this relationship over a broad range of soil concentrations (about 0 to 0.4 mg/g).

Some evidence was found to suggest that phenanthrene dissolves off less readily at low soil concentrations (<0.06 mg/g) as a pure compound than in a mixture with pyrene. However, this trend was not consistent at higher soil concentrations.

Little difference in dissolution was observed between phenanthrene and pyrene mixtures applied to the soils using two different methods. The first being the mixing of the pure compound coated soils and the second being the coating of soil with a mixture of the two compounds.

Such findings have possible practical applications in terms of soil cleanup. The results suggest that at lower chemical soil concentrations, more water is required to remove the same mass of chemical per mass unit soil than at higher soil concentrations, and there may be limits to the soil concentration attainable using water washing.

References

- Backhus, D.A., P.M. Gschwend and S. J. Eisenreich, 1995, "Sorption of Hydrophobic Organic Chemicals to Inorganic Surfaces: A Critical Review", *Environ. Sci. Technol.*, in review.
- Banerjee, S., 1984, "Solubility of Organic Mixtures in Water", *Environ. Sci. Technol.*, 18:587-591.
- Bewley, R., B. Ellis, P. Theile, I. Viney and J. Rees, 1989, "Microbial Clean-up of Contaminated Soil", *Chemistry & Industry (London)*, 778-783.
- Brusseau, M.L., 1991, "Cooperative Sorption of Organic Chemicals in Systems Composed of Low Organic Carbon Aquifer Materials", *Environ. Sci. Technol.*, 25:1747-1752.
- Chiou, P.V. and D.W. Schmedding, 1982, "Partitioning of Organic Compounds in Octanol-Water Systems", *Environ. Sci. Technol.*, 16:4-9.
- Eaganhouse, R.P. and J.A. Calder, 1976, "The Solubility of Medium Molecular Weight Aromatic Hydrocarbons and the Effects of Hydrocarbon Co-Solutes and Salinity", *Geochimica et Cosmochimica Acta.*, 40:555-561.
- Feenstra, S., D.M. Mackay, and J.A. Cherry, 1991, "A Method for Assessing Residual NAPL Based on Organic Chemical Concentrations in Soil Samples", *Ground Water Monitoring Review*, 11:128-135.
- Fetter, C.W. 1993. *Contaminant Hydrogeology*. Macmillan Publishing Co, New York, NY.
- Jahan, K., 1993, Ph.D. thesis. "Biodegradation of Phenanthrene in Soils in the Presence of Surfactants". University of Minnesota.
- Karickhoff, S.W., D.S. Brown, and T.A. Scott, 1979, "Sorption of Hydrophobic Pollutants on Natural Sediments", *Water Research*, 13:241-248.
- Kiemele, M.J. and S.R. Schmidt. 1991. *Basic Statistics: Tools for Continuous Improvement*. Air Academy Press, Colorado Springs, CO.
- Lane, W.F. and R.C. Loehr, 1995, "Predicting Aqueous Concentrations of Polynuclear Aromatic Hydrocarbons in Complex Mixtures", *Water Environment Research*, 67:169-173.
- Lee, L.S., M. Hagwall, J.J. Delfino and P.S.C. Rao., 1992, "Partitioning of Polycyclic Aromatic Hydrocarbons from Diesel Fuel into Water", *Environ. Sci. Technol.*, 26:2104-2110.
- Lee, L.S., P.S.C. Rao and I. Okuda, 1992, "Equilibrium Partitioning of Polycyclic Aromatic Hydrocarbons from Coal Tar into Water", *Environ. Sci. Technol.*, 26:2110-2115.

Liu, Z., S. Laha and R.G. Luthy, 1991, "Surfactant Solubilization of Polycyclic Aromatic Hydrocarbon Compounds in Soil-Water Suspensions", *Wat. Sci. Tech.*, 23:475-485.

Mackay, D., W.Y. Shiu, and K.C. Ma, 1992. *Illustrated Handbook of Physical-Chemical Properties and Environmental Fate for Organic Chemicals Vol II*. Lewis Publishers, Chelsea, MI.

Mader, B., 1994-95, Personal Communications.

MacIntyre, W.G. and P.O. deFur, 1985, "The Effect of Hydrocarbon Mixtures on Adsorption of Substituted Naphthalenes by Clay and Sediment from Water", *Chemosphere*, 14:103-110.

Maier, W.J., 1994-95, Personal Communications.

Maier, W.J. et al. 1994 Final Report., "Bioremediation of Contaminated Soils - Aquifers on Reilly Site in St. Louis Park, Minnesota", University of Minnesota.

Nelson, M.D., and W.J. Maier, 1995, "In Situ Bioremediation of Creosote Impacted Soil and Ground Water", *Proceedings 50th Purdue Industrial Waste Conference*, Purdue University, W. Lafayette, Indiana.

Park, K.S., R.C. Sims and R.R. Dupont, 1990, "Transformation of PAHs in Soil Systems", *Journ. of Env. Eng.*, 116:632-640.

Peters, C.A. and R.G. Luthy, 1993, "Coal Tar Dissolution in Water-Miscible Solvents: Experimental Evaluation", *Environ. Sci. Technol.*, 27:2831-2843.

Schwarzenbach, R.P., P.M. Gschwend, and D.M. Imboden. 1993. *Environmental Organic Chemistry*. John Wiley & Sons, Inc., New York, NY.

Smidt, D.P., 1995, M.S. thesis. "Sorption of Mixtures of Polycyclic Aromatic Hydrocarbons on Low Organic Content Soils". University of Minnesota.

Sugatt, R.H., D.P. O'Grady, and S. Banerjee, 1984, "Toxicity of Organic Mixtures Saturated in Water to *Daphnia Magna*. Effect of Compositional Changes.", *Chemosphere.*, 13:11-18.

Susurla, S., G.V. Bhoskar, and S.M. Rao Bhamidimarri, 1992, "Competitive Adsorption of Phenoxy Herbicide Chemical in Soil", *Wat. Sci. Tech.*, 26:2121-2124.

Tam, E., 1994-95, Personal Communications.

Verschuere, Karel, 1983. *Handbook of Environmental Data on Organic Chemicals*. Van Nostrand Reinhold Company, New York, NY.

Voice, T.C. and W.J. Weber Jr., 1983, "Sorption of Hydrophobic Compounds by Sediments, Soils and Suspended Solids - I", *Water Research*, 17:1433-1441.

Weber, W.J., 1972. *Physicochemical Processes for Water Quality Control*. John Wiley & Sons, Inc., New York, NY.

**WATER WASHING OF POLYCYCLIC AROMATIC
HYDROCARBONS FROM SOILS**

**A THESIS
SUBMITTED TO THE FACULTY OF THE GRADUATE SCHOOL OF THE
UNIVERSITY OF MINNESOTA**

BY

PAULA ANNE THORSON

**IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF
MASTER OF SCIENCE IN CIVIL ENGINEERING**

AUGUST, 1995

ACKNOWLEDGMENTS

First of all I would like to thank Dr. Walter J. Maier for all of his help and guidance in getting me through this program. His support and assistance were greatly appreciated, especially on those days when I questioned my choice of the plan A option. I would also like to thank Professor Malcolm Hepworth and Professor Fay Thompson for the time and effort that they contributed as members of my thesis review committee. Eric Tam deserves special thanks for his extensive assistance in the lab, for without it my thesis would not have been possible. His talks were inspiring as well.

I would also like to thank Dave Kopchynski for helping me in the lab and in my classes, and Steve Dodge for assisting me until the military required his services. I also appreciated Brian Mader's valuable advice and willingness to answer my many questions.

My family and friends deserve special thanks for putting up with me and keeping me sane. They also gave me something to look forward to when I took time off. My roommate and fellow Air Force officer, Carrie Bischel, deserves special recognition for tolerating me and for making my graduate school experience a positive one.

The prompt assistance that I received from Sergeant Riley and the other members of the ROTC staff in dealing with military matters was greatly appreciated. Their help made it possible to focus on my studies with fewer outside distractions. I would also like to thank the US Air Force for the scholarship that made it possible for me to attend graduate school.

Finally, I would like to thank God for giving me the strength to make it through and for blessing me with all of those mentioned above.

ABSTRACT

Dissolution studies were carried out using batch operations with soils that were prepared in the laboratory. The soil used was Jordan sand (fraction organic carbon (foc) <0.0001). The sand was coated with varying concentrations of phenanthrene and pyrene, both of which are polycyclic aromatic hydrocarbons (PAHs). Hexane was used to dissolve the chemical and then coat the sand. Double distilled water with a pH of about 5 was used to wash the various coated sands over a series of days. They were given four days to equilibrate before the water was analyzed and replaced with new water.

It was found that lower solubilities were obtained for phenanthrene at lower soil concentrations. Strong linear correlations were observed over short ranges of about 0.1 mg/g or less. However there was evidence that a nonlinear function would be necessary to describe this relationship over a broad range of soil concentrations (about 0 to 0.4 mg/g) due to decreasing slopes with increasing soil concentrations.

Some evidence was found to suggest that phenanthrene dissolves off less readily at low soil concentrations (<0.06 mg/g) as a pure compound than in a mixture with pyrene. However, this trend was not consistent at higher soil concentrations.

Little difference in dissolution was observed between phenanthrene and pyrene mixtures applied to the soils in two different methods. The first being the mixing of the pure compound coated soils and the second being the coating of soil with a mixture of the two compounds.

Finally, such findings have possible practical applications in terms of soil cleanup. The results suggest that at lower chemical soil concentrations, more water is required to remove the same mass of chemical per mass unit soil than at higher soil concentrations. There is also some evidence that there may be limits to how clean a soil can get with mere water washing.

TABLE OF CONTENTS

	Page
Chapter 1	
<i>Introduction and Literature Review</i>	
Introduction	1
Literature Review	6
Chapter 2	
<i>Design of Experiment</i>	
Preliminary Investigations	12
Chapter 3	
<i>Experimental and Analytical Methods</i>	
Experimental Methods	15
Analytical Methods	24
Chapter 4	
<i>Methods of Data Analysis and Correlation</i>	28
Chapter 5	
<i>Results and Discussion</i>	
Background	30
Reproducibility of Experimental Results	31
Results	
Solution Concentrations in Sequential Water Washes	31
Soil Concentrations in Sequential Water Washes	40
Analysis of Water and Soil Concentration Data	47
Discussion of Combined Data Sets	57
Comparison to Desorption Study	71
Overall Mass Balance	73
Practical Implications	77
Chapter 6	
<i>Conclusions</i>	
Conclusions Regarding Original Questions	81
Other Conclusions	82
References	83

LIST OF TABLES

Table		Page
5.1	PT#2 Summary of Chemical Masses	74
5.2	PT#3 Summary of Chemical Masses	75
5.3	PT#4 Summary of Chemical Masses	76

LIST OF FIGURES

Figure	Page
2.1 Pyrene Equilibration	14
2.2 Photolysis Check	14
5.1a PT#2 Solution Concentrations in Sequential Water Washes (Phen A)	34
5.1b PT#2 Solution Concentrations in Sequential Water Washes (Phen AsBs)	34
5.1c PT#2 Solution Concentrations in Sequential Water Washes (Phen AB)	34
5.2a PT#2 Solution Concentrations in Sequential Water Washes (Pyr B)	35
5.2b PT#2 Solution Concentrations in Sequential Water Washes (Pyr AsBs)	35
5.2c PT#2 Solution Concentrations in Sequential Water Washes (Pyr AB)	35
5.3a PT#3 Solution Concentrations in Sequential Water Washes (Phen A)	36
5.3b PT#3 Solution Concentrations in Sequential Water Washes (Phen AsBs)	36
5.3c PT#3 Solution Concentrations in Sequential Water Washes (Phen AB)	36
5.4a PT#3 Solution Concentrations in Sequential Water Washes (Pyr B)	37
5.4b PT#3 Solution Concentrations in Sequential Water Washes (Pyr AsBs)	37
5.4c PT#3 Solution Concentrations in Sequential Water Washes (Pyr AB)	37
5.5a PT#4 Solution Concentrations in Sequential Water Washes (Phen A)	38
5.5b PT#4 Solution Concentrations in Sequential Water Washes (Phen AsBs)	38
5.5c PT#4 Solution Concentrations in Sequential Water Washes (Phen AB)	38
5.6a PT#4 Solution Concentrations in Sequential Water Washes (Pyr B)	39
5.6b PT#4 Solution Concentrations in Sequential Water Washes (Pyr AsBs)	39
5.6c PT#4 Solution Concentrations in Sequential Water Washes (Pyr AB)	39
5.7a PT#2 Soil Concentrations in Sequential Water Washes (Phen A)	41
5.7b PT#2 Soil Concentrations in Sequential Water Washes (Phen AsBs)	41
5.7c PT#2 Soil Concentrations in Sequential Water Washes (Phen AB)	41
5.8a PT#2 Soil Concentrations in Sequential Water Washes (Pyr B)	42
5.8b PT#2 Soil Concentrations in Sequential Water Washes (Pyr AsBs)	42
5.8c PT#2 Soil Concentrations in Sequential Water Washes (Pyr AB)	42
5.9a PT#3 Soil Concentrations in Sequential Water Washes (Phen A)	43
5.9b PT#3 Soil Concentrations in Sequential Water Washes (Phen AsBs)	43
5.9c PT#3 Soil Concentrations in Sequential Water Washes (Phen AB)	43
5.10a PT#3 Soil Concentrations in Sequential Water Washes (Pyr B)	44
5.10b PT#3 Soil Concentrations in Sequential Water Washes (Pyr AsBs)	44
5.10c PT#3 Soil Concentrations in Sequential Water Washes (Pyr AB)	44
5.11a PT#4 Soil Concentrations in Sequential Water Washes (Phen A)	45
5.11b PT#4 Soil Concentrations in Sequential Water Washes (Phen AsBs)	45
5.11c PT#4 Soil Concentrations in Sequential Water Washes (Phen AB)	45
5.12a PT#4 Soil Concentrations in Sequential Water Washes (Pyr B)	46
5.12b PT#4 Soil Concentrations in Sequential Water Washes (Pyr AsBs)	46
5.12c PT#4 Soil Concentrations in Sequential Water Washes (Pyr AB)	46
5.13a PT#2 Water Concentration Vs Soil Concentration (Phen A)	51
5.13b PT#2 Water Concentration Vs Soil Concentration (Phen AsBs)	51
5.13c PT#2 Water Concentration Vs Soil Concentration (Phen AB)	51
5.14a PT#2 Water Concentration Vs Soil Concentration (Pyr B)	52
5.14b PT#2 Water Concentration Vs Soil Concentration (Pyr AsBs)	52
5.14c PT#2 Water Concentration Vs Soil Concentration (Pyr AB)	52
5.15a PT#3 Water Concentration Vs Soil Concentration (Phen A)	53
5.15b PT#3 Water Concentration Vs Soil Concentration (Phen AsBs)	53

Figure	Page
5.15c PT#3 Water Concentration Vs Soil Concentration (Phen AB)	53
5.16a PT#3 Water Concentration Vs Soil Concentration (Pyr B)	54
5.16b PT#3 Water Concentration Vs Soil Concentration (Pyr AsBs)	54
5.16c PT#3 Water Concentration Vs Soil Concentration (Pyr AB)	54
5.17a PT#4 Water Concentration Vs Soil Concentration (Phen A)	55
5.17b PT#4 Water Concentration Vs Soil Concentration (Phen AsBs)	55
5.17c PT#4 Water Concentration Vs Soil Concentration (Phen AB)	55
5.18a PT#4 Water Concentration Vs Soil Concentration (Pyr B)	56
5.18b PT#4 Water Concentration Vs Soil Concentration (Pyr AsBs)	56
5.18c PT#4 Water Concentration Vs Soil Concentration (Pyr AB)	56
5.19a Water Concentration Vs Soil Concentration (Pure Phenanthrene) (PT#2 Phen A, PT#3 Phen A, PT#4 Phen A)	59
5.19b Water Concentration Vs Soil Concentration (Pure Phenanthrene for all Experiments)	59
5.20a Water Concentration Vs Soil Concentration (Pure Pyrene) (PT#2, PT#3, PT#4)	60
5.20b Water Concentration Vs Soil Concentration (Pure Pyrene for all Experiments)	60
5.21a Water Concentration Vs Soil Concentration (Equal Initial Phenanthrene Masses) (PT#2 Phen A, PT#3 Phen AsBs, PT#3 Phen AB)	64
5.21b Water Concentration Vs Soil Concentration (Equal Initial Phenanthrene Masses) (PT#3 Phen A, PT#4 Phen AsBs, PT#4 Phen AB)	64
5.21c Figure 5.21a and Figure 5.21b Combined (linear fit)	65
5.21d Figure 5.21a and Figure 5.21b Combined (log fit)	65
5.22a PT#2 Water Concentration Vs Soil Concentration (Equal Chemical Masses Applied Differently) (Phen AsBs, Phen AB)	68
5.22b PT#3 Water Concentration Vs Soil Concentration (Equal Chemical Masses Applied Differently) (Phen AsBs, Phen AB)	68
5.22c PT#4 Water Concentration Vs Soil Concentration (Equal Chemical Masses Applied Differently) (Phen AsBs, Phen AB)	68
5.23a PT#2 Water Concentration Vs Soil Concentration (Equal Chemical Masses Applied Differently) (Pyr AsBs, Pyr AB)	69
5.23b PT#3 Water Concentration Vs Soil Concentration (Equal Chemical Masses Applied Differently) (Pyr AsBs, Pyr AB)	69
5.23c PT#4 Water Concentration Vs Soil Concentration (Equal Chemical Masses Applied Differently) (Pyr AsBs, Pyr AB)	69
5.24a Water Concentration Vs Soil Concentration (Equal Chemical Masses Applied Differently) (All 3 Experiments Combined) (Phen AsBs, Phen AB)	70
5.24b Water Concentration Vs Soil Concentration (Equal Chemical Masses Applied Differently) (Pyr AsBs, Pyr AB)	70
5.25a Comparison of Dissolution and Desorption Data	72
5.25b Close-up of Generated Desorption Curve	73
5.26a Pore Volumes Vs Treatment Goal (PhA)	80
5.26b Pore Volumes Vs Treatment Goal (PhAsBs)	80
5.26c Pore Volumes Vs Treatment Goal (PhAB)	80

Chapter 1

INTRODUCTION AND LITERATURE REVIEW

INTRODUCTION

Hydrophobic organic compounds (HOCs) have caused considerable concern with regards to the contamination of natural soil-water systems. Once these chemicals get into the soil they are very difficult to remove either by soil washing or microbial degradation (Liu et al., 1991).

Accidental spills as well as past land disposal practices have lead to the contamination of many subsurface environments with HOCs. In order to develop improved methods for cleaning up these sites, it is necessary to have a thorough understanding of the processes affecting their fate in the subsurface. Ultimately the goal is to develop quantitative descriptions in the form of mathematical models. Such models would be useful in assessing the effectiveness and costs of removing subsurface contaminants as well as for the evaluation of remediation alternatives (Backhus et al., 1995).

Polycyclic aromatic hydrocarbons (PAHs) are a group of HOCs which are produced by high-temperature industrial processes such as petroleum refining, coke production, wood preservation, and synthetic oil and gas production. They are of critical environmental and public health concern for a number of reasons which include chronic health effects (carcinogenicity), microbial recalcitrance, high bioaccumulation potential, and low removal efficiencies in traditional wastewater treatment processes (Park et al., 1990). Several PAHs are included on the US Environmental Protection Agency (EPA) list of priority pollutants (Lee et al., 1992).

A number of soil and water contamination problems have resulted from improper disposal of coal tar from manufactured gas plants (MGPs) and from wood treating

facilities. Many of these sites pose serious problems because they act as long term sources of groundwater pollution.

One of the primary factors controlling the movement, dispersion, and ultimately cleanup of the higher molecular weight PAH's is their low water solubility. In general, highly soluble contaminants are more readily removed than the slightly soluble ones. A related question is whether the physical distribution of chemicals in contaminated soils affects their availability for dissolution. Quantitative information about the potential for solubilizing these chemicals in the soil environment is therefore needed.

Initial physical distribution of chemicals in the soil matrix is the result of soil properties as well as the physical chemical composition of the contaminants. They can enter subsurface environments as solutes in contaminated water or as separate non-aqueous phase mixtures such as creosote or diesel fuel. Chemicals entering as solutes are likely to be retained by adsorption on soil surfaces. Non-aqueous phase mixtures of slightly soluble organics that percolate into the subsurface are likely be retained in the soil matrix in the form of coatings on soil surfaces and as occlusions in pore spaces after displacing the groundwater. Both mechanisms of entry and distribution in the soil may be involved concurrently.

Adsorption is the result of partitioning of solubilized chemicals from the water phase to the soil. Adsorption desorption processes have been studied extensively (Backhus et al., 1995; Smidt, 1995; Brusseau, 1991; Karickhoff et al., 1979; Susarla et al., 1992; Voice and Weber, 1983; MacIntyre and deFur, 1985; Jahan, 1993). Adsorption usually results in relatively low accumulations of contaminants which do not impact hydraulic conductivity significantly. By contrast, the introduction of separate phase nonaqueous fluids may result in complete displacement of the water from pore spaces allowing for intimate contact between the organic phase and the mineral surfaces. As regards transport and ultimate physical distribution of non-aqueous fluids in soils, viscosity, specific gravity,

and miscibility with water are seen as critical variables. Ultimate distribution in the soil may be in the form of thin film coatings on mineral surfaces or in the form of occlusions in selected pore spaces depending on the physical properties of the contaminant source as well as soil properties. Obviously the extent of dissolution of chemicals in contaminated soils will be affected by their physical distribution because it determines the extent of contact with groundwater flow through the soil. Physical distribution of chemicals in pores and on surfaces is therefore an important parameter as regards quantitative descriptions of how the retained chemicals can ultimately be flushed out of the soil or removed by insitu biodegradation.

The assumption that organic contaminant concentrations in the aqueous phase leaving a coal tar source would be equal to their corresponding pure compound aqueous solubilities has been a popular one in the past. It was based on the assumptions that each chemical is present as a separate pure phase to justify the assumption of ideal solution theory, and that saturated solutions would obtain equilibrium after sufficient contact time with the water phase. Most complex wastes however such as coal tar, diesel, and gasoline, consist of mixtures of contaminants, many of which are PAHs (Lee et al., 1992). Furthermore, the original mixtures are usually in the form of liquids. However, they tend to weather with time and ultimately become quasi solid phases as a result of the loss of low molecular weight species. This process is akin to the change of tar into asphalt. It is interesting to note that residues of creosote observed in weathered soils have a similar physical appearance to asphaltic materials (Maier et al., 1994). It is therefore not surprising that observed solubilities of individual chemicals from such mixtures are usually much lower than that of the individual pure compounds. This is an important factor as regards clean up of sites by water flushing as well as insitu biodegradation.

One popular means of cleaning contaminated soil is the pump-and-treat method. This involves the removal of ground water that contains dissolved chemicals so that it can

be treated at the surface to eliminate the contaminants. It has been observed in conventional pump and treat operations that there tends to be an initial rapid decline in the concentration of contaminants in the water being removed by the system. In a study of sixteen sites in the United States where ground water pumping was practiced, it was reported that if the initial water phase concentration of contaminants was high ($>1000\mu\text{g/L}$), then pumping could achieve reductions of contaminant concentrations of 90 to 99 % before leveling occurred (C.B. Doty and C.C. Davis, 1991). However, at sites where the initial concentration was less than $1000\mu\text{g/L}$, leveling occurred before a 90% reduction was accomplished (Fetter, 1993). It is unclear whether such results are due to insufficient contact of the water with the soil or solubility limitations of the chemical resulting from contact with the soil.

In one study done by Nelson (1995) of the rates of leaching of PAHs from soil columns taken from a creosote contaminated site, it was found that PAH effluent concentrations were as little as ten percent of aqueous solubility. Comparable results have been seen with creosote contaminated soils from the Reilly Tar Superfund Site (Maier et al., 1994). Results from column studies as well as batch reactor contacting studies gave similar results (Smidt, 1995). By contrast, Jahan (1993) reported results from columns aimed at measuring solubilization of phenanthrene from a sandy soil precoated with phenanthrene. She found that when flushing a column of phenanthrene coated low organic content aquifer material (Jordan sand) with water, she got high initial effluent concentrations around that of phenanthrene's solubility. However, after successive washings (about 20 pore volume displacements) effluent concentrations were found to decrease considerably. This slower release with time was attributed to the decrease in readily available surface area of coated phenanthrene to the flowing water phase (Jahan, 1993).

This research was aimed at obtaining a more precise understanding of the factors that impact dissolution of solid phase PAH's coated on soil surfaces. The study was designed to address the following questions:

- a) What is the contact time needed to achieve equilibrium solubility (S_{equ}) of selected PAH's coated on low organic content aquifer material?
- b) Is the value of S_{equ} dependent on the mass of chemical remaining on the soil?
- c) How does the presence of mixtures of PAH's affect their solubility in comparison to pure compounds?
- d) Is there a difference in solubility from soils coated with mixtures of chemicals as opposed to single PAHs coated on sands which are mixed?

The studies were conducted in batch reactors to measure solubilities after equilibration. Two slightly soluble PAH model compounds were used in the research, phenanthrene and pyrene. Phenanthrene is a three ring aromatic hydrocarbon with a chemical equation of $C_{14}H_{10}$. When present in the dry state, it exists as dry colorless leaflets. It has a molecular weight of 178.22, a melting point of 100°C , a boiling point of 340°C , a specific gravity of 1.025, and a solubility of about 0.816 mg/L at 21°C . Pyrene is a four ring aromatic hydrocarbon with a chemical equation of $C_{16}H_{10}$. It has a molecular weight of 202.26, a melting point of $149 - 151^{\circ}\text{C}$, and a solubility of about 0.16 mg/L at 26°C (Verschueren, 1983). Some preliminary testing was also carried out on benzo(a)anthracene, which has a much lower solubility, but these tests were abandoned because of analytical problems. Jordan sand ($\text{foc} < .0001$) was coated in the lab with hexane solutions of each pure PAH and mixtures of the two chemicals. Coated sands were then equilibrated with water to measure solubilities.

LITERATURE REVIEW

Polycyclic aromatic hydrocarbons (PAHs) are hydrophobic organic compounds readily sorbed onto soil (Liu et al., 1991). The US EPA has listed sixteen of them as priority pollutants to be monitored in industrial effluents largely due to their carcinogenicity (Bewley et al., 1989).

Near the source of contamination, one of the main processes controlling the release of organic chemicals is its solubility in water. It has often been assumed in the past that organic contaminant concentrations in the aqueous phase in contact with a source would be equal to or at least approach their corresponding pure compound aqueous solubilities. This assumption may be reasonable if the source material is composed of a single contaminant, but may not be appropriate if the source material is a mixture of chemicals which is the case for most sources such as coal tar, diesel, and gasoline (Lee et al., 1992). Of the components in these mixtures, compounds of lower molecular mass will tend to evaporate and degrade more readily, leaving residuals consisting of higher molecular mass components that are quasi-solids at ambient conditions (Lee et al., 1992).

The aqueous solubility of coal tar has been discussed by several investigators in recent years in an effort to understand groundwater contamination at coal tar sites. One approach to correlating data on the aqueous solubilities of mixtures is based on Raoult's law (Chiou and Schmedding, 1982; Banerjee, 1984; Cline et al., 1991; Feenstra et al., 1991; Peters and Luthy, 1993; Lane and Loehr, 1995). Raoult's law states that for an ideal two-phase liquid mixture at equilibrium, the mole fraction of a compound in one liquid phase can be estimated from the compound's mole fraction in the other liquid phase (Lane and Loehr, 1995). This method was used in research done by Peters and Luthy (1993) in order to estimate the bulk solubility of coal tar as a pseudocomponent. Their method and equations are explained below.

Equal fugacities, defined as a molecule's "urge" to flee a system (Schwarzenbach, 1993), characterize the equilibrium solute partitioning in liquid-liquid systems. When the assumption is made that the solute behaves ideally in both the aqueous and coal tar phases, the equilibrium relation for solute i becomes:

$$x_i^w = x_i^{ct} x_i^{wL} \quad (\text{eq. 1.1})$$

Where

- x_i^w = mole fraction of solute i in the water phase
- x_i^{ct} = mole fraction of i in the coal tar phase
- x_i^{wL} = mole fraction equivalent of the aqueous solubility of pure liquid i .

With the assumption that the aqueous phase is sufficiently dilute so that the volume of the solution is approximately equal to that of pure water, the aqueous concentration can also be expressed in terms of mass concentrations. An equation similar to the first can be written:

$$C_i^w = x_i^{ct} S_i^L \quad (\text{eq. 1.2})$$

Where

- C_i^w = mass concentration of i in the water phase (mg/L)
- S_i^L = aqueous solubility of pure liquid i (mg/L)
- $x_i^{ct} = (\text{wt}\%_i/100)(\text{MW}_{CT}/\text{MW}_i)$

Where

- $\text{wt}\%_i$ is the weight percent of i in the coal tar
- MW_{CT} = average molecular weight of the coal tar
- MW_i = molecular weight of compound i

As pointed out by Peters and Luthy (1993), Raoult's law pertains to mixtures of liquids and probably should be modified to correlate data on the solubilities of quasi-solid phases. Since many PAHs are solids in the pure state at ambient temperatures, S_i^L should be modified to reflect the differences in the thermodynamic energy between liquid and solid states. An expression that relates S_i^L to S_i^S , the pure solid aqueous solubility at the system

temperature, can be derived from the thermodynamics of solid-liquid equilibrium where the standard state in the liquid phase is defined as the pure subcooled liquid at the temperature of the solution. When this relationship is applied to the previous equation, the following equation results:

$$C_i^w = x_i^{ct} S_i^s (f^L/f^S)_{\text{pure } I} \quad (\text{eq. 1.3})$$

Where

$(f^L/f^S)_{\text{pure } I}$ = the ratio of the pure component fugacities in the subcooled liquid and the solid states

Schwarzenbach (1993) refers to this fugacity ratio as the activity of the compound. That is, it is a measure of how active a compound is in a given state compared to its reference state. Fugacity ratios are sometimes available in literature and can also be approximated by an expression that accounts for the free-energy change between the liquid and the solid state, using a constant entropy of fusion for organic compounds (Peters and Luthy, 1993).

A similar method was used by Lane and Loehr (1995) in a paper on predicting the aqueous concentrations of PAHs in complex mixtures. They assumed that soil organic matter, which typically dominates sorption of hydrophobic PAH compounds, is included in the "liquid" coal tar matrix. According to them, the aqueous concentration (c_w) can be predicted from the following equation:

$$c_w = x_t S_{\text{SCL}} \quad (\text{eq. 1.4})$$

Where

x_t = the mole fraction in the tar phase
 S_{SCL} = the supercooled liquid solubility

The partitioning model assumes two liquid phases and that is why the supercooled liquid solubility is used. In that way, each compound partitioning between the liquid phases (tar and water) acts as a liquid solute rather than a solid. Since most reference values for aqueous solubilities are given for crystalline solutes, the crystalline solubility (S_C) can be converted to the liquid solubility by the following:

$$\log S_{SCL} = \log S_C + 0.01(MP - 25) \quad (\text{eq. 1.5})$$

Where

MP = the compound's melting point ($^{\circ}\text{C}$)

The first equation can then be rewritten to directly estimate the aqueous phase concentration:

$$C_{w,\text{mg/L}} = c_t(MW_t)S_{SCL,\text{molar}} \quad (\text{eq. 1.6})$$

Where

c_t = the compound concentration in the tar phase (mg/kg)

MW_t = the average molecular weight of the tar matrix

It was found in this particular study that aqueous concentrations predicted by Raoult's law were generally within an order of magnitude of the measured concentrations (Lane and Loehr, 1995).

In a study done by Lee et al. (1992) with diesel fuel, the assumption of ideal behavior was made and Raoult's law was applied. The following equation was applied in that study to solve for the equilibrium aqueous-phase concentrations:

$$C_w = C_{df}MW_{df}S_l/\rho_{df} \quad (\text{eq. 1.7})$$

Where

C_{df} = the concentration of the component in the diesel fuel

MW_{df} = molecular weight of the diesel fuel

S_l = supercooled liquid solubility of the component of interest

ρ_{df} = density of the diesel fuel

In this study, the diesel fuel-water partitioning of several PAHs, all solids in their standard state, was well described by employing supercooled liquid solubilities and assuming ideal behavior (Lee et al., 1992).

In yet another study performed by Lee et al. (1992) on coal tar composition, the following equation was applied:

$$C_w = x_o S_1 \quad (\text{eq. 1.8})$$

Where

C_w = the chemical's concentration in the aqueous phase (mol/L)

x_o = the mole fraction of the chemical in the organic phase

S_1 = aqueous solubility of the pure liquid chemical (mol/L) or the hypothetical supercooled liquid solubility for compounds that are solid in their standard state

It was concluded that the application of Raoult's law and the assumption of ideal behavior may be adequate to predict the concentration of PAHs in groundwater in contact with a coal tar source since good agreement for a majority of PAHs within a factor of two was found (Lee et al., 1992).

Of course if most of the solvents in a spill have evaporated, the result might be closer to a noninteracting solid-solid mixture. These are poorly understood but Banerjee (1984) used this equation to describe it:

$$\log S = aX + b(\text{mp}) + c$$

Where

S = solubility of the hydrophobic solid

X = a parameter such a total surface area, molar volume, the octanol-water partition coefficient, or the boiling point

mp = melting point in $^{\circ}\text{C}$

Since solubility is dependent upon melting point, it makes sense that impure compounds which usually have lower melting points than those of pure compounds will have correspondingly higher solubilities. Banerjee found in his work however that the solubility

in water of solid mixtures were relatively independent of composition. Eaganhouse and Calder (1976) on the other hand found that solubilities of medium molecular weight aromatic hydrocarbons were both enhanced and reduced due to the presence of other similar compounds.

Another mechanism to consider is that of sorption which is a term used to describe the process of a solute's interfacial accumulation between two distinct phases, particularly when one phase is a solid (Weber, 1972). HOC hydrophobicity, sorbent type, and surface area seem to be the primary factors controlling the sorption of HOC to inorganic surfaces with fraction organic carbon (foc) less than 0.001. Limited data suggest that solution conditions like pH, ionic strength, temperature, and HOC concentration seem to have only a small effect on measured sorption coefficients (Backhus et al., 1995).

Few studies have examined sorption of HOCs in the presence of other HOCs. It was found by MacIntyre and deFur (1985) that sorption of HOCs to a particular substrate was almost independent and non-competitive. The adsorption coefficients varied generally by less than a factor of two. Brusseau (1991) found enhanced sorption of naphthalene and p-xylene (by a factor of 1.5 to 3) to a low organic carbon aquifer material in the presence of tetrachloroethylene at saturation. There is the possibility that the sorption of tetrachloroethylene to the low organic carbon sorbent effectively increased both the quantity and quality of the foc, therefore increasing the observed sorption of the other HOC. It is particularly important to quantify this effect when examining the fate of HOCs at the many hazardous waste sites contaminated by HOC mixtures such as coal tar, fuels, etc. However, due to limited data and conflicting results, further work is necessary to determine the magnitude of multiple HOC effects on sorption (Backhus et al., 1995).

Chapter 2

DESIGN OF EXPERIMENT

The objective of the bench scale study was to measure the extent of dissolution of phenanthrene and pyrene that had previously been coated on Jordan sand in the lab. The experiments were designed to measure the mass of chemical dissolved as a function of

- 1) the type of chemical coated on the sand (phenanthrene or pyrene)
- 2) the mass of chemical coated on the sand
- 3) the time of contact between sand and water to establish steady state if not true equilibrium
- 4) the effect of coating the sand with mixtures of phenanthrene and pyrene

The soil in this research is representative of clean uncontaminated low organic content soil. It was 100% Jordan sand which had a fraction organic carbon (foc) of <0.0001 (mass of carbon/total mass). The soil fraction used for all experiments was that passing through sieve #30 and retained on sieve #100. The soil was prepared by rinsing it multiple times with water and then letting it dry in the oven overnight at 105°C . The sand was stirred the next day and returned to the oven. On the following day it was removed, placed in a large beaker, and covered with aluminum foil. Three samples of the sieved and washed sand were analyzed by the University of Minnesota Department of Soil Science Research Analytical Laboratory for measurement of foc. The reported foc of all samples was <0.0001 .

PRELIMINARY INVESTIGATIONS

A short term equilibration study was done using pyrene coated sand to determine the length of time necessary for equilibrium to be established. One gram of sand coated with 0.2mg/g of pyrene was placed in each of three 40 ml glass vials (borosilicate, 40ml,

.125 in septa-liner, I-Chem, lot# 3029013). Forty ml of double distilled water was then added to each and they were placed in the refrigerator on an orbit shaker at $21 \pm 1^{\circ}\text{C}$. A two ml sample was removed from each vial each day for six days and analyzed using the solid phase microextraction method (SPME) and gas chromatograph. Details of the analytical procedure are given in Chapter 3. After about four days, little change in water concentration was observed as shown in figure 2.1. Based on these results, all subsequent tests were carried out for four days in order to establish stable conditions. Since the solubility of phenanthrene is ten times that of pyrene, it was assumed that it would reach an equilibrium state before the pyrene did and therefore it was not tested and the same equilibration time was used.

Although all the vials were stored in the dark, there was some concern that there might be some photolytic degradation occurring during sample removal which tended to result in 1/2 to 1 hours of exposure to the room light. In order to test for this, the following experiment was performed.

A water solution containing 0.2 mg/L phenanthrene and 0.02 mg/L pyrene was made up and 40 ml was placed in a 40ml vial with an aluminum foil coated cap. Two 2ml samples were removed and analyzed using SPME at time = 0. The vial was left on the counter and two more samples were removed at time = 30 min and a final two at time = 60 min. No detectable change in peak area with time was observed as shown in Figure 2.2.

Solid phase microextraction (SPME) combined with gas chromatography(GC) analysis was used to extract and analyze the samples. It was also decided that hexane extractions would be done of the initial coated sands and the washed sands in order to obtain a mass balance for each chemical.

Figure 2.1: Pyrene Equilibration

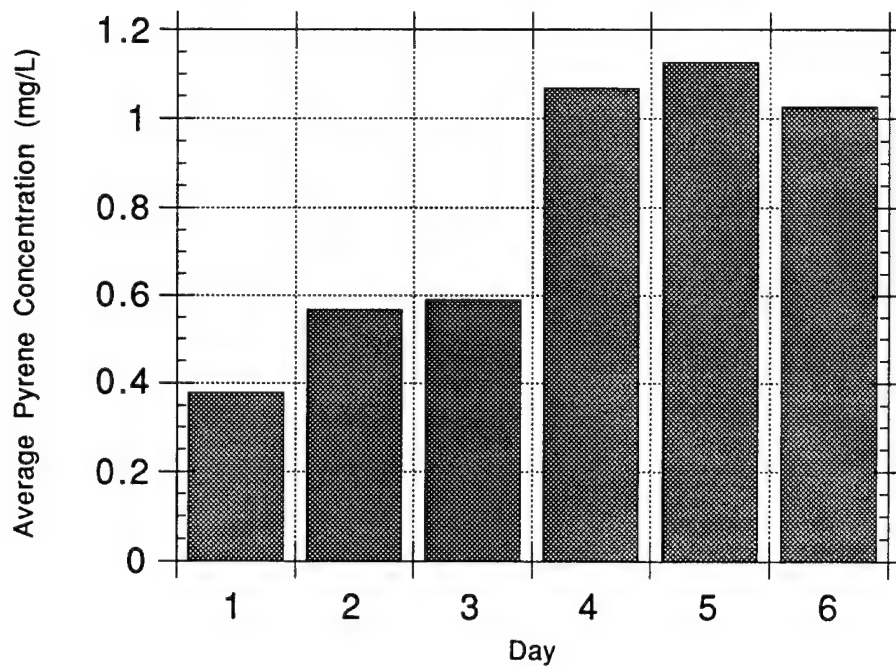
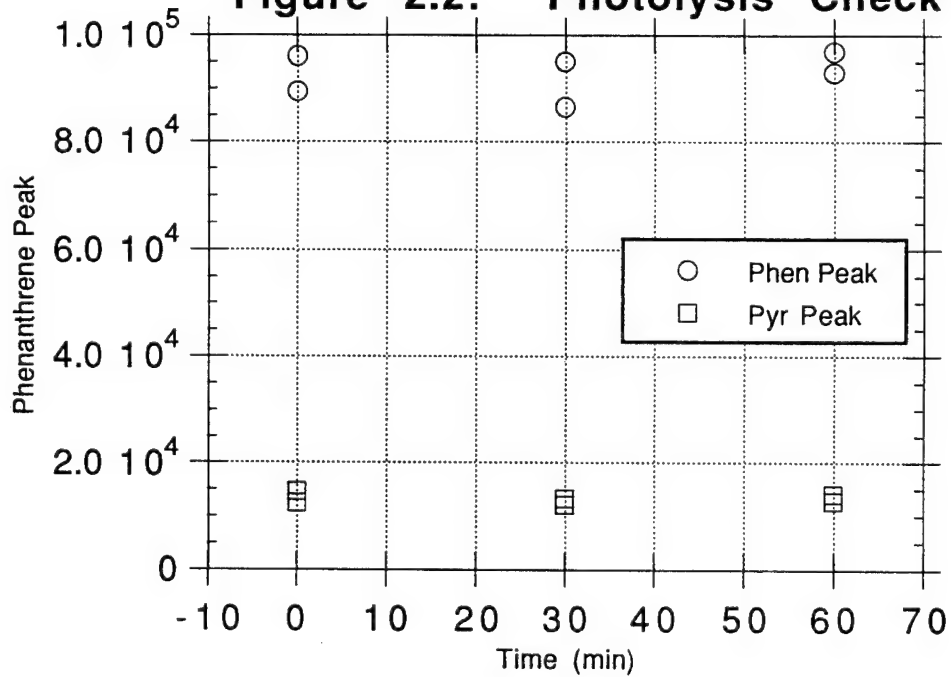


Figure 2.2: Photolysis Check



Chapter 3

EXPERIMENTAL AND ANALYTICAL METHODS

EXPERIMENTAL METHODS

Soil Preparation/Cleaning:

Jordan aquifer soil was sieved and that which passed through a #30 sieve and was retained on a #100 sieve was collected in a large beaker. Approximately 1 kg was collected. The soil was then rinsed in a large metal bowl with deionized water, stirred by hand, and drained. This was repeated several times until the drained water was essentially clear. This took about 45 minutes. The bowl full of soil was then placed in the oven at 105° C overnight. The next day the sand was stirred and placed back into the oven. The sand was removed on the following day, covered with aluminum foil, and allowed to cool to room temperature. It was later placed in a large beaker, covered with aluminum foil, and stored on the counter.

Coating Soil with Pure PAHs:

Twelve clean 40ml beakers and 12 glass stir rods were rinsed with hexane and allowed to dry. Six of the beakers were then filled with 50mg of "clean" Jordan aquifer soil. The following amounts of chemicals were placed in the remaining beakers:

<u>Beaker</u>	<u>Chemical</u>	<u>Amount (mg)</u>	<u>Nominal mass of chemical on soil (mg/g)</u>
1	phenanthrene	20.0	0.4
2	phenanthrene	10.0	0.2
3	phenanthrene	5.0	0.1
4	pyrene	20.0	0.4
5	pyrene	10.0	0.2
6	pyrene	5.0	0.1

Note: The phenanthrene was from Supelco, 98% purity, cat#4-8569. The pyrene was also from Supelco, 97% purity, cat#4-8570.

Twelve ml of hexane (Optima™, HPLC grade, Fisher cat#A454-1) was added to the first beaker containing chemical. The solution was then stirred until all of the chemical was dissolved. Then 50g of soil was added to the beaker while still stirring so that all of the soil was made to come in contact with the solution. The decision to use 12ml was based on the assumption of a porosity of 0.35 and calculations which lead to the determination that this would result essentially in complete saturation of the soil. The same procedure was followed for the remaining 5 beakers of chemical. All of the beakers with stir rods were then left overnight so that the hexane could evaporate. The next day the dry sands were removed from the hood and each was stirred for about 2 minutes. Each was poured into a clean beaker and covered with aluminum foil and placed in a shoe box on the counter.

Mass Balance for Coating Soil:

There was some concern about how much chemical stuck to the beaker and stir rod instead of the soil and therefore an attempt was made to quantify this. In effect, two 5ml aliquots of hexane were used to wash the beakers and glass stirrers after the sand had been removed and this wash was analyzed for PAHs as described below.

Six 10ml disposable glass test tubes were marked at the 10ml point using a graduated pipet (borosilicate, 10ml, disposable, sterile, Baxter, cat#53281-724) and double distilled water. They were then emptied of the water and put in the oven to dry at 105° C. Twelve 2ml GC vials were labeled to correspond with the different beakers. Tapping and mild air blowing from the nozzle in the hood were used to remove any remaining soil from the first beaker and stir rod. A graduated pipet was used to rinse the beaker and stir rod with 5ml of hexane. This hexane was then poured into the test tube and then it was repeated with another 5ml. After both rinses were in the test tube, hexane was added until it reached the 10ml mark. A 2ml disposable pipet (Pasteur, borosilicate

glass, VWR Scientific Inc., cat#14673-043) was used to mix the hexane by squeezing it up and down four times. Then between 1 and 2ml was placed in each of two 2ml GC vials. The same procedure was followed for the remaining beakers and stir rods. The samples were then placed in the refrigerator where they remained until they were analyzed.

The results of this analysis accounted for less than 15% of the mass of phenanthrene unaccounted for on the coated soils based on the hexane extractions of the "dry" soils. There are a number of other possible explanations for the loss of chemical in the coating process. It is possible that some evaporation occurred of the chemical, there may have also been errors in measuring the chemical amounts into the hexane solution used to coat the soils, the soil coating may have been less uniform than we expected and therefore the three samples tested for initial coating may have been low in comparison to other samples, and finally the hexane calibration may have been slightly off therefore predicting lower initial coating concentrations than reality. Stirring the soil continuously until dry may have been one way to ensure a more uniform coating. Also, analyzing more samples of coated soil would give a better indication of the average coating.

PT Test Run #1 Method:

The septums were removed from fourteen 40ml vials (borosilicate, .125 in septaliner, I-Chem, lot#3029013) and covered with aluminum foil and replaced. Two vials were made up of each of the following samples:

<u>40ml Vials</u>	<u>Nominal mass of chemically coated sand added to each vial</u>
1 (A&B)	1.00 g of 0.4 mg phenanthrene/g soil
2 (A&B)	1.00 g of 0.2 mg phenanthrene/g soil
3 (A&B)	1.00 g of 0.1 mg phenanthrene/g soil
4 (A&B)	1.00 g of 0.4 mg pyrene/g soil
5 (A&B)	1.00 g of 0.2 mg pyrene/g soil
6 (A&B)	1.00 g of 0.1 mg pyrene/g soil
7 (A&B)	1.00 g of hexane coated soil

Note: As shown above, controls using soil treated with pure hexane were also tested.

Using a disposable 10ml graduated pipet (borosilicate, sterile, Baxter, cat#53281-724), 40ml of double distilled water was added to each vial. The mass of each vial was recorded before and after the addition of the water. The vials were then placed in a rack and placed on an orbit shaker (Lab-Line) on 65RPM in a refrigerator at $21 \pm 1^{\circ}\text{C}$. The samples were removed from the shaker on the following day (after about 22.5 hrs of shaking). Two ml GC vials (clear, crimp, wide opening, Hewlet Packard, part #5181-3375) were labeled and a small Teflon coated stir rod was placed in each. Two ml from each large vial (1A and 1B) was placed in the corresponding GC vial using a graduated pipet and then it was capped. The pH was taken of the samples and recorded. The remainder of the water in each of the large vials was pipeted out and discarded. As much as possible was removed without sucking up the sand. The caps were replaced loosely on bottles 1A and 1B. The same procedure was then followed for all large vials.

After removing the water, double distilled water was added to each large vial with a graduated pipet until it reached the same mass as in the previous washing step ($\pm 0.02\text{g}$). Its cap was then placed on it tightly and it was returned to its rack. This was then repeated for the remaining vials. Once all of the vials were done, they were placed back in the refrigerator on the shaker just as they had been the previous day. This same procedure was followed for the next 4 days. The GC vials were placed in the refrigerator as soon as they were all prepared. All of the samples were analyzed on the day that they were extracted.

Calibration Check for PT#1:

During PT Test Run #1, a calibration check was performed each day to see if the calibration of the GC remained consistent. The equipment was rinsed with methanol and placed in the oven. Six 2ml GC vials were labeled and a small Teflon stir bar was placed in each. A 500ml volumetric flask was filled with double distilled water. A large Teflon stir bar was placed in a 500ml beaker on a magnetic stirrer (model PC-320, Corning) and the

500ml of double distilled water was poured in. The stirrer was turned to about 4 to get a good vortex. The stock solution was removed from the refrigerator. It was made up of 80mg phenanthrene, 8mg pyrene, and 20ml methanol (for a concentration of 4.0mg/ml phenanthrene and 0.4mg/ml pyrene).

100 μ L of stock solution were injected into the water with a 100 μ L syringe at a rate of about 10 μ L/min for a total of about 10 minutes. The stock solution was recapped and placed back in the refrigerator. The beaker containing the solution was covered with aluminum foil and allowed to stir for 15 minutes. It was then allowed to stand for 2 minutes and was checked for a film or particles on the top of the solution. No film and very few tiny particles were ever observed. It was then stirred for 1 hour covered with aluminum foil. It was then allowed to sit again for 2 minutes and again observed for specs or a film. The solution was then stirred slowly.

Fifteen ml of double distilled water was placed in each of five 25ml bottles. Two ml of the solution (concentration of 0.8mg/l phenanthrene, 0.08mg/l pyrene) was placed in each of two 2ml GC vials. Then 5ml of the solution was pipeted into the first bottle which was swished around for about 40 seconds and then pipeted up and down twice. The same pipet was then used to transfer 2ml of this solution (concentration of 0.2mg/l phenanthrene, 0.02mg/l pyrene) into 2 of the GC vials and then 5ml of it into the second bottle. The same procedure was then followed for this bottle creating a concentration of 0.05mg/l of phenanthrene and 0.005mg/l of pyrene. These solutions were then analyzed each day prior to analyzing the samples.

Hexane Extraction of Prepared Soils for PT#1:

The overall procedure was designed to extract two 1 gram samples of soil with two 5ml aliquots of hexane. Fourteen 40ml I-Chem vials were rinsed with about 2.5ml of hexane and allowed to dry under the hood. The septums in the caps of the bottles were

then covered with aluminum foil to avoid adsorption to the Teflon. One gram of each of the prepared soils was placed in 2 of each of the vials and labeled accordingly. The weight of each vial was recorded. Five ml of hexane was then added to each of the vials using the dispensing device attached to the bottle. The weight of each vial was recorded after the addition of the hexane as well. Each vial was swirled gently before being placed in the rack and then they were all placed in the refrigerator on the shaker overnight at 70 RPM.

The vials were removed from the shaker on the following day and the weight of each was recorded before hexane removal. Then 2ml disposable pipets were used to remove the hexane from each vial and 1 to 2ml was placed in each of two corresponding GC vials. The remainder of the hexane was removed and then the vial was weighed again. As much hexane as possible was removed without sucking up the sand. Five ml of hexane was then added to the vial and it was swirled a bit and replaced in the rack. The same procedure was followed for the next two days.

Hexane Extraction of Experimental Soils from PT#1:

The same procedure was followed as for the hexane extraction of the prepared soils for the "wet" soils that remained after the execution of PT#1. The only exception is that it was necessary to air dry the soils under the hood for three days prior to the extraction.

GC Calibration for Hexane Solutions:

First a stock solution containing 1mg/ml of phenanthrene and 1mg/ml of pyrene in hexane was made up and diluted to 0.1mg/ml of phenanthrene and 0.1mg/ml of pyrene. Dilutions were then made of the following concentrations in mg/ml (0.025, 0.00625, 0.0015625, 0.000390625). Two samples at each concentration were tested in order to create a calibration curve for the GC. They were linear in all cases.

Coating Soil with PAH Mixtures:

The same method was used for coating the soil as for PT #1 but the following chemical combinations were used:

<u>Beaker</u>	<u>Chemical</u>	<u>Amount (mg)</u>	<u>Nominal mass of chemical on sand (mg/g)</u>
8	phenanthrene	2.5	0.05
8	pyrene	5.0	0.10
9	phenanthrene	5.0	0.10
9	pyrene	5.0	0.10
10	phenanthrene	10.0	0.20
10	pyrene	5.0	0.10

PT Test Run #2 Method:

Essentially the same procedure was followed as for PT Test Run #1 with the following exceptions. The samples were allowed to equilibrate for four days instead of for only one, three vials of each type were prepared instead of two, and some vials received mixtures of soil or soils impregnated with mixtures of chemicals as shown below:

<u>Vial #</u>	<u>Nominal mass of chemically coated sand added to each vial</u>
A (1,2&3)	1.00 g of 0.1 mg/g phenanthrene soil
B (1,2&3)	1.00 g of 0.2mg/g pyrene soil
AsBs (1,2&3)	0.50 g of 0.1 mg/g phenanthrene soil and 0.50 g of 0.2 mg/g pyrene soil
AB (1,2&3)	1.00 g of (0.5 mg/g phenanthrene and 0.1 mg/g pyrene) soil
control	1.00 g of hexane coated soil

The longer time for equilibration was used in order to ensure adequate time for steady state to be obtained. The use of three replicating bottles was designed to provide more precise test results.

PT Test Run #3 Method:

The same procedure was followed as for PT Test Run #2 but with the following samples:

<u>Vial #</u>	<u>Nominal mass of chemically coated sand added to each vial</u>
A (1,2&3)	1.00 g of 0.2 mg/g phenanthrene soil
B (1,2&3)	1.00 g of 0.2 mg/g pyrene soil
AsBs (1,2&3)	0.50 g of 0.2 mg/g phenanthrene soil and 0.50 g of 0.2 mg/g pyrene soil
AB (1,2&3)	1.00 g of (0.1 mg/g phenanthrene and 0.1 mg/g pyrene) soil
control	1.00 g of hexane coated soil

PT Test Run #4 Method:

The same procedure was followed as for PT Test Run # 2 but with the following samples:

<u>Vial #</u>	<u>Nominal mass of chemically coated sand added to each vial</u>
A (1,2&3)	1.00 g of 0.4 mg/g phenanthrene soil
B (1,2&3)	1.00 g of 0.2 mg/g pyrene soil
AsBs (1,2&3)	0.50 g of 0.4 mg/g phenanthrene soil 0.50 g of 0.2 mg/g pyrene soil
AB (1,2&3)	1.00 g of (0.2 mg/g phenanthrene and 0.1mg/g pyrene) soil
control	1.00 g of hexane coated soil

Calibration Check for PT#2-4:

The same procedure was followed as for PT#1 with the following exceptions. A glass stir bar was used (made in the University of Minnesota glass shop) instead of the Teflon one because of concerns about PAH adsorption to Teflon, new stock solution was made up, disposable test tubes were used instead of bottles, a ratio of 6ml:2ml instead of 15ml:5ml was used for dilutions, and only one vial of each concentration was made. Also, the calibration checks were performed every other day due to time constraints.

Hexane Extraction of Prepared Soils for PT#2-4:

The same procedure was followed as for PT#1 with the exception that three samples of each kind were tested.

Hexane Extraction of Experimental Soils for PT#2-4:

The same procedure was followed as for PT#1 with the exception that they took four days to dry.

ANALYTICAL METHODS

Solid Phase MicroExtraction (SPME) Method:

a. Equipment:

SPME fiber assembly, 7 μ m polydimethylsiloxane coating (Supelco, cat#5-7302)

SPME holder (Supelco, cat#5-7330)

b. Procedure:

First the sample was removed from the refrigerator. The sample in all cases consisted of a 2ml sample in a 2ml GC vial with a small Teflon stir bar.

For extraction, the general sampling procedure found in catalogue No. 5-7330 (Instructions for the Supelco™ Solid Phase MicroExtraction Fiber Holder for Manual Use) was used with slight modifications shown below:

- 1) The needle depth was adjusted by rotating the needle guide so that the septum piercing needle would pierce the septum. (Note: The catalogue recommended not contacting the sample but since our vials were filled to the top this was impossible. Some wicking did occur as a result but the only negative effect observed from this was the frequent need to reignite the FID on the GC.)
- 2) With the fiber withdrawn, the septum of the sample vial was pierced and the magnetic stirrer it was sitting on was turned on.
- 3) The plunger was pushed down until the fiber was exposed and turned until the retaining screw was fully to the left in the horizontal slot. The holder was then held in place with a lab stand device. A small box was placed around the vial to eliminate possible photolytic effects.
- 4) The fiber remained in the sample for 20.0 minutes. This time was arrived at in previous tests which determined it to be sufficient.
- 5) The fiber was retracted by turning the plunger counterclockwise until the plunger popped up. The sample was then ready for GC injection.

Gas Chromatograph Analysis (for SPME):

EPA method 8000 (General Chromatography) and EPA method 8100 (GC Analysis of Polynuclear Aromatic Hydrocarbons) were followed.

a. External Standard Calibration

Calibration standards were prepared by first dissolving the phenanthrene and pyrene in a methanol stock solution and then dissolving it into water. A minimum of three concentration levels were prepared within the range of expected values (It was found that additional lower concentration levels had little effect on the resulting calibration line). The peak areas were compared against the concentrations of the extracted solutions and a linear fit was developed for each chemical.

b. GC Analysis Parameters

One injection from each sample was performed on the GC under the following conditions:

GC	Hewlett Packard 5890
Integrator	HP 3396
Column	HP-5, 25m x 0.2 mm x 0.33 μ m
Detector	FID
Carrier Gas	Hydrogen, 2 ml/min
Initial Temp.	60 ^o C
Initial Time	3 min.
Rate	10 ^o /min
Final Temp.	320 ^o C
Final Time	0 min.

c. Procedure:

For injection, the general sampling procedure found in catalogue No. 5-7330 (Instructions for the Supelco™ Solid Phase MicroExtraction Fiber Holder for Manual Use) was used with slight modifications shown below:

- 1) With the fiber retracted, the needle guide was adjusted to a height that would expose the fiber to the hottest part of the injector port when the plunger was pushed down.

- 2) The GC inlet septum was pierced with the septum piercing needle and the holder was pushed down until the end of the needle guide touched the injector septum nut.
- 3) Immediately the plunger was pushed all the way down with one hand while the other started the integrator. The plunger was again rotated to lock it in place. The holder was supported with a small wrench.
- 4) The fiber was exposed for 15 minutes.
- 5) The fiber was withdrawn into the septum-piercing needle by turning the plunger counterclockwise until the plunger popped up.
- 6) The septum piercing needle was removed from the injection port immediately.

Gas Chromatograph Analysis (for hexane solutions):

EPA method 8000 (General Chromatography) and EPA method 8100 (GC Analysis of Polynuclear Aromatic Hydrocarbons) were followed.

a. External Standard Calibration

Calibration standards were prepared by dissolving the phenanthrene and pyrene in Optima grade hexane (Fisher Scientific). A minimum of five concentration levels were prepared. The concentration levels began near but not below the detection limit of the instrument. The rest were within the range of expected values. The peak areas were compared against the concentrations of the injected solutions and a linear fit was developed for each chemical.

b. GC Analysis Parameters

One injection from each sample was performed on the GC under the following conditions:

GC	Hewlett Packard 5890 w/ auto sampler
Integrator	HP 3396
Column	HP-5, 25m x 0.2 mm x 0.33 μ m
Detector	FID
Carrier Gas	Hydrogen, 2 ml/min
Initial Temp.	60 ^o C
Initial Time	3 min.
Rate	10 ^o /min
Final Temp.	320 ^o C
Final Time	0 min.
Injection vol.	1 μ L

Chapter 4

METHODS OF DATA ANALYSIS AND CORRELATION

Mass Balance

Overall mass balances were calculated for each test using the measured initial concentration of chemical on the soil, measurements of the aqueous concentration, and the measured mass of chemical remaining on the soil at the end. The following equation was used to calculate the stepwise reduction in soil concentration after each wash. Soil concentrations after five washes were also calculated.

$$S_n = S_{n-1} - W_n(V)/M \quad (\text{eq. 4.1})$$

Where

S_n = soil concentration during sample n (mg/g)

S_{n-1} = soil concentration during the previous sample (mg/g)

note: For the first sample, the soil concentration as determined by the hexane extraction of the coated soil was used.

W_n = water concentration during sample n (mg/L)

V = volume of water equilibrated with sample n (L) (This was 0.04L)

M = mass of soil present (g) (This was 1 g)

Adsorption of chemical to the glass or aluminum foil lined septum in the bottle was assumed negligible. This was based on the fact that adsorption to these surfaces is generally small, the sand has a much greater surface area and therefore any adsorption would be small in comparison, and finally there is no practical way to measure this parameter for this experiment. Summary tables of the results of the overall mass balances can be seen in Chapter 5.

Plots

Plots were made of "Solution Concentrations in Sequential Water Washes" to determine if any trends existed. Plots of "Soil Concentrations in Sequential Water Washes"

were created for the same reason. Plots were then made of "Water Concentration Vs Soil Concentration" to determine if a relationship existed between the two variables. Linear regressions were performed on these plots to determine the relationship(if any) in each case. Two-sample hypothesis tests of the mean were performed to determine whether results between pure compounds and mixtures were statistically significant.

Chapter 5

RESULTS AND DISCUSSION

BACKGROUND

Batch water contacting operations were conducted on sand coated with different amounts of phenanthrene and pyrene as pure compounds as well as mixtures. The chemicals were coated onto pure Jordan sand ($foc < .0001$) using hexane as a solubilizer. The actual amounts of chemical that adhered to the soil was determined by hexane extraction of the soils after they had been coated. Samples of coated sand were sequentially contacted with 5 batches of pure water and allowed to equilibrate on a shaker. The water was tested and replaced with new water every four days to determine the concentration of water in equilibrium with the soil. All experiments were done in triplicate. It was determined that four days was sufficient to reach near steady state solution concentrations. Therefore it was considered equilibrium for the purpose of this analysis. Results from three tests run, PT#2, PT#3, and PT#4 which have progressively higher phenanthrene content while keeping pyrene content the same, are discussed in this section. Complete descriptions of test methods and analytical procedures are presented in Chapters 2 and 3.

The objectives of these experiments were to:

- 1) Determine whether the dissolution of a chemical from a low organic soil is dependent upon the amount of chemical remaining on that soil.
- 2) Determine if the presence of mixtures of chemicals affects their dissolution in comparison to pure compounds.
- 3) Determine if there is a difference between the dissolution of chemicals from soils coated with mixtures of chemicals versus mixtures of soils each coated with a single chemical.

REPRODUCIBILITY OF EXPERIMENTAL RESULTS

All experiments were done in triplicate in order to measure the reproducibility of the results. They were all performed at the same time. Error bars for each water concentration point are included on the plots which represent one standard deviation from the mean. In the case of the plots of "Soil Concentrations in Sequential Water Washes", the chemical concentration on the soil on day zero represents the initial soil concentration as determined by hexane extraction of three coated soil samples. These error bars then demonstrate the reproducibility of the soil coating method. Since later soil concentrations were calculated using the previous ones, their error was additive. The standard deviation from the soil extraction was added to the standard deviation derived from the water wash which was also used in this calculation. One can see by the error bars that overall reproducibility was good for the water washings. However, the error bars for the hexane extractions are somewhat larger and are likely due to somewhat uneven coating of the soils.

SOLUTION CONCENTRATIONS IN SEQUENTIAL WATER WASHES

Measured water concentrations for each of the five batches of water were plotted versus wash number to see if any trends existed for all three of the experiments (see Figures 5.1a - 5.6c). The procedure used to label the plots is as follows. Phen A represents phenanthrene alone just as Pyr B represents pyrene alone. Phen AsBs represents the phenanthrene concentration present in the mixture where sand coated with phenanthrene alone was mixed with sand coated with pyrene alone. Pyr AsBs represents the pyrene present in the same mixture. Finally, Phen AB represents the phenanthrene concentration where a mixture of phenanthrene and pyrene were coated on the soil together. In the same way Pyr AB represents the pyrene present in the same mixture. This convention holds true for all plots.

It can be seen from these plots that in experiments PT#2 and PT#3, where the initial soil concentrations are lower, there is a progressive decrease in aqueous phenanthrene concentration over the course of the experiments (see Figures 5.1a,b,c and 5.3a,b,c). A less pronounced decrease was also observed in PT#4 (see Figures 5.5a,b,c). The first two points of PT#4 are significantly higher than the rest. They are close to what is expected for saturation concentrations of phenanthrene. Typical values quoted in literature range from about 0.8 to 1.6 mg/L at 25°C with an average around 1.24 mg/L (Mackay et al., 1992). Maximum concentrations reported in previous studies in our laboratory at 22°C (Jahan, 1994) using phenanthrene from the same supplier show a solubility in the range of 0.8-0.9 mg/L. The value of 1.16 measured for water wash number 2 in test PT#4 is particularly high and furthermore is higher than the water wash number 1 sample. It is not clear why the wash number 2 samples in PT#4 are elevated compared to the wash number 1 samples. The fact that it was observed in all three soil tests (PhenA, PhenAsBs, and Phen AB) suggests that this trend was caused by some unrecognized difference in test procedures. Review of the test data shows that the water wash number 2 samples had inadvertently been exposed to an extra day of contact with the water without shaking. It is therefore possible that the four day equilibration procedure was insufficient for testing soil with higher concentrations of phenanthrene. Although this same incident should have affected the number 3 water washes for PT#2 and PT#3, the data for these did not show unusual variations. Therefore perhaps the effect is greater for soils with greater concentrations.

The plots for pyrene, (shown in Figures 5.2a,b,c; 5.4a,b,c; 5.6a,b,c) show that the solution concentrations remained essentially the same in all five batches of water. Furthermore, the observed concentrations are close to saturation values reported in the literature. Typical values quoted in literature for pyrene solubility range from about 0.1 to 0.17 mg/L with an average value of about 0.14 at 25°C (Mackay et al., 1992). The

solubility at 21°C would therefore be expected to be somewhat lower. The concentrations observed here ranged from about 0.075 to about 0.10 mg/ml.

Some of the water wash number 2 test data in PT#3 and PT#4 also show a slight increase in pyrene concentration over the respective water wash number 1 samples. In these experiments, the soil pyrene concentrations were not changed, therefore it does not support the explanation that higher soil concentrations are responsible for this discrepancy unless it is a carryover effect from the higher phenanthrene soil concentrations used in these experiments. The fact that these increases occurred in a number of samples suggests that there may have been some change in procedure that was not recognized. The fact that the wash number 2 samples are higher because they had an extra day of contacting (particularly without shaking) cannot be eliminated as a possible cause even though it is inconsistent with other test data obtained in this study. Another possible, and perhaps more likely, explanation would be that the calibration was slightly off that day and caused a consistent over estimate of the water concentration.

Figure 5.1a: PT#2 Solution Concentrations
In Sequential Water Washes

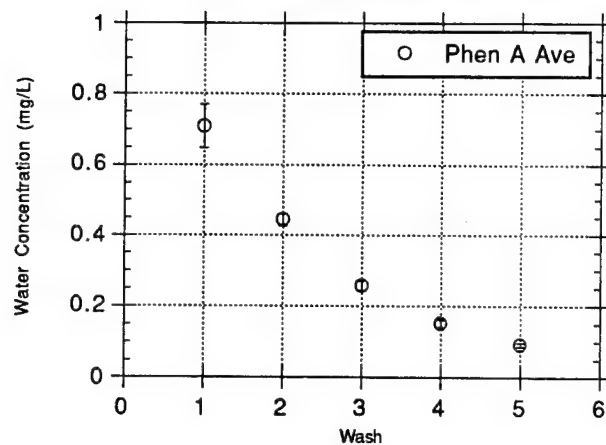


Figure 5.1b: PT #2 Solution Concentrations
in Sequential Water Washes

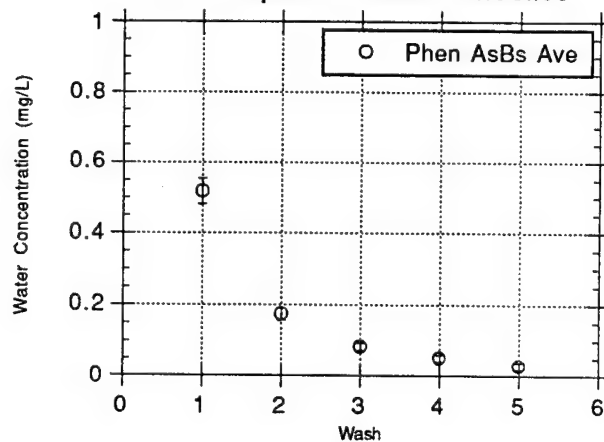
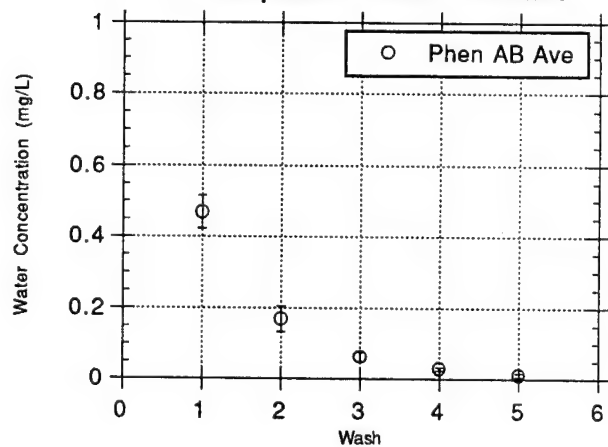
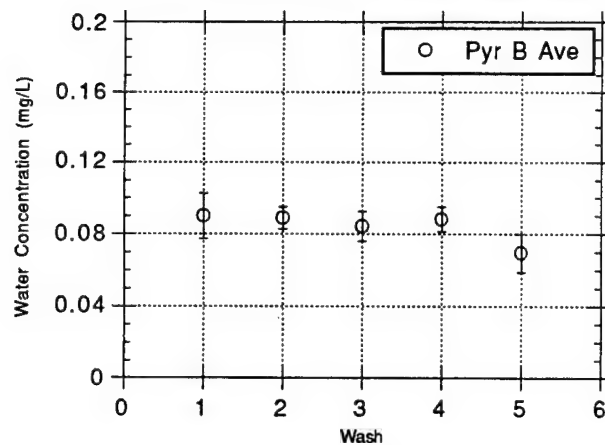


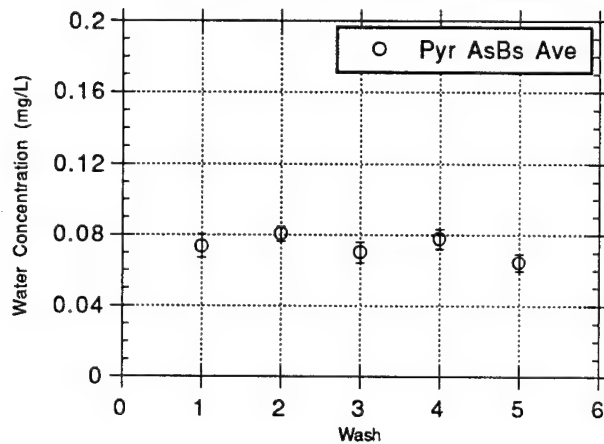
Figure 5.1c: PT#2 Solution Concentrations
In Sequential Water Washes



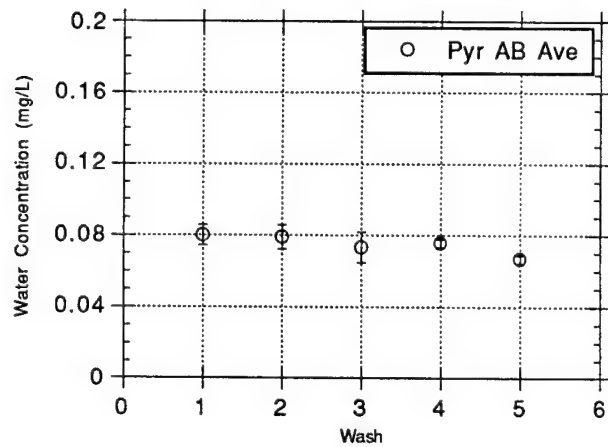
**Figure 5.2a: PT#2 Solution Concentrations
in Sequential Water Washes**



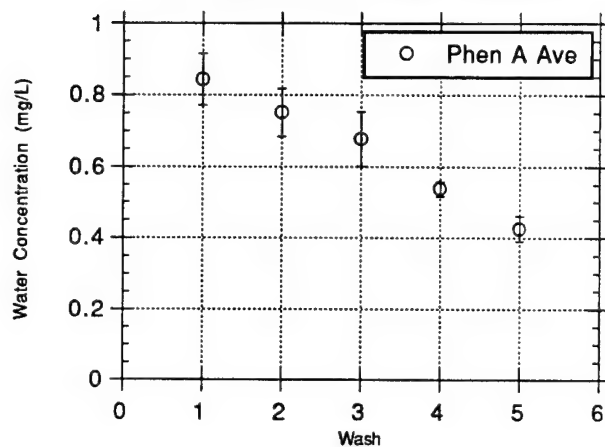
**Figure 5.2b: PT#2 Solution Concentrations
in Sequential Water Washes**



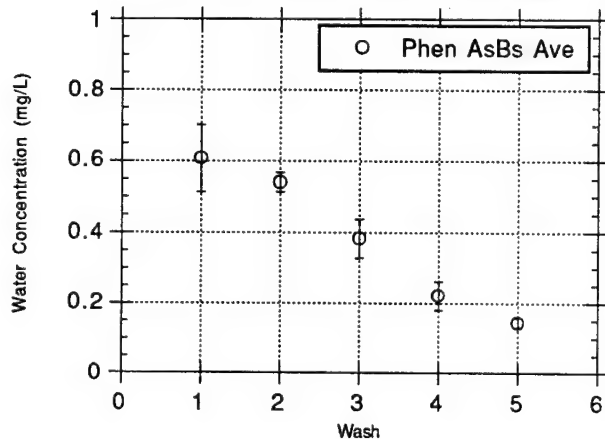
**Figure 5.2c: PT#2 Solution Concentrations
in Sequential Water Washes**



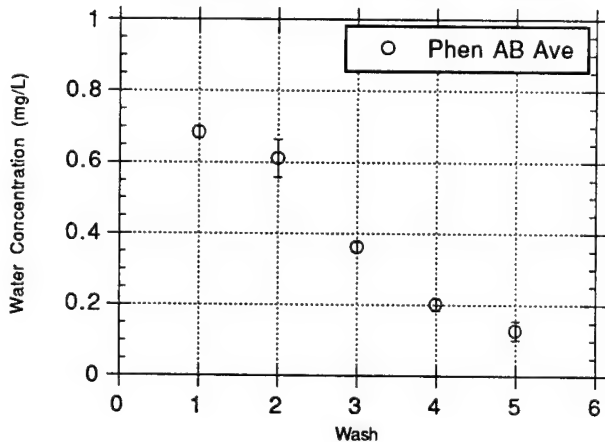
**Figure 5.3a: PT#3 Solution Concentrations
in Sequential Water Washes**



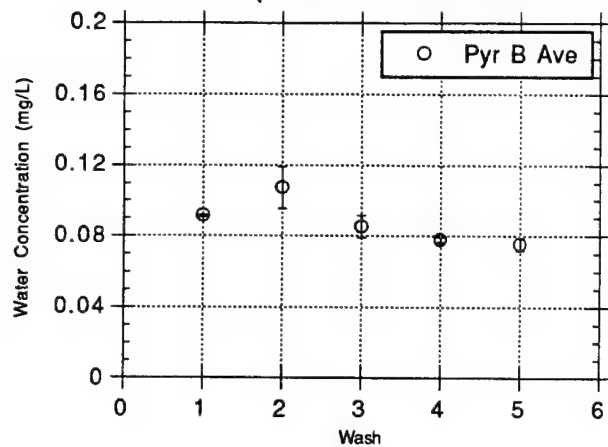
**Figure 5.3b: PT#3 Solution Concentrations
in Sequential Water Washes**



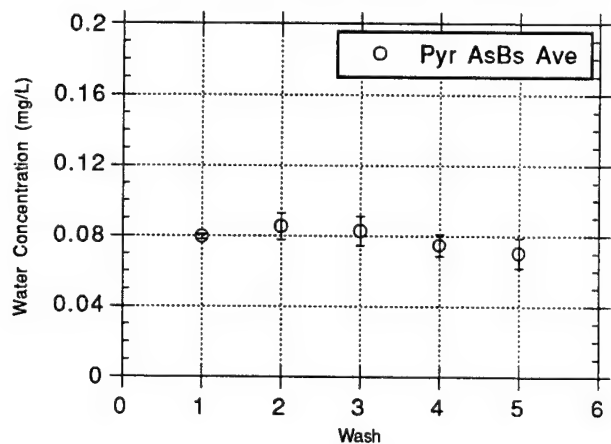
**Figure 5.3c: PT#3 Solution Concentrations
in Sequential Water Washes**



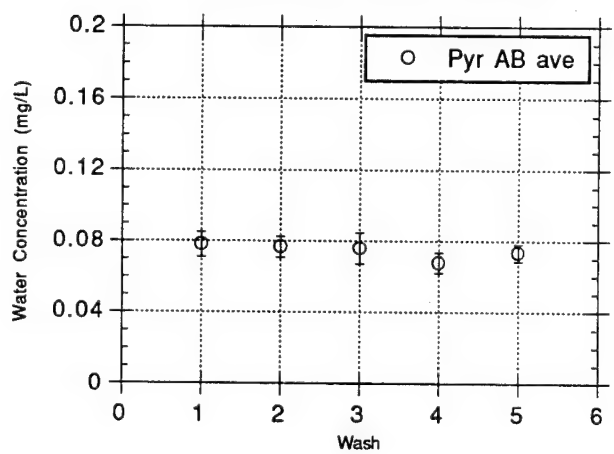
**Figure 5.4a: PT#3 Solution Concentrations
in Sequential Water Washes**



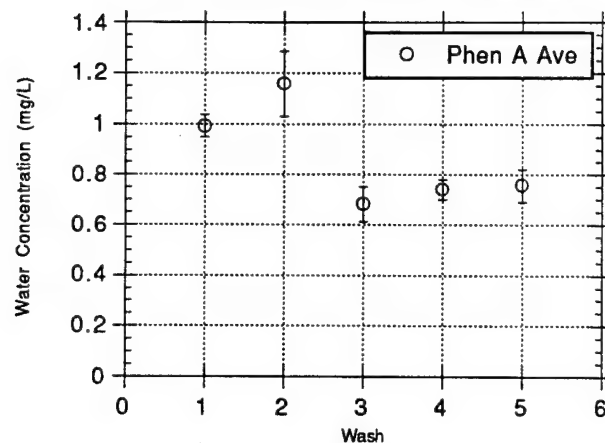
**Figure 5.4b: PT#3 Solution Concentrations
in Sequential Water Washes**



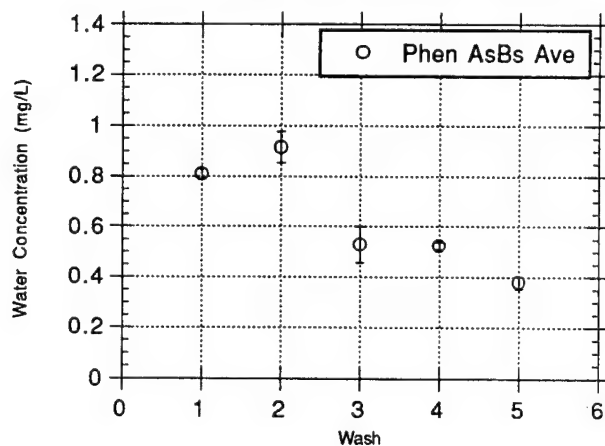
**Figure 5.4c: PT#3 Solution Concentrations
in Sequential Water Washes**



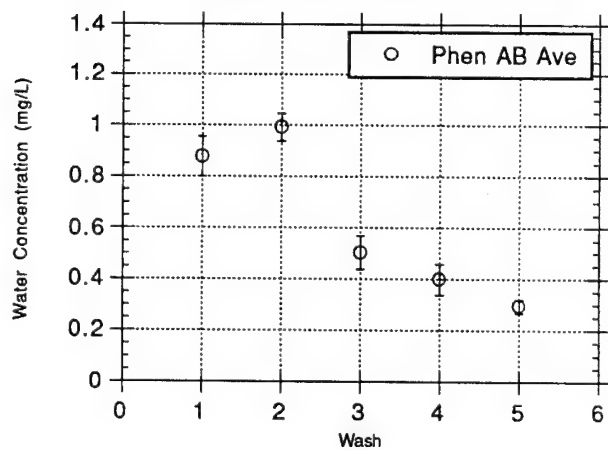
**Figure 5.5a: PT#4 Solution Concentrations
in Sequential Water Washes**



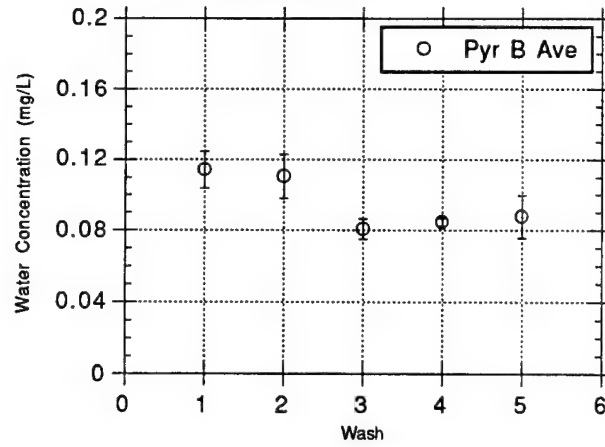
**Figure 5.5b: PT#4 Solution Concentrations
in Sequential Water Washes**



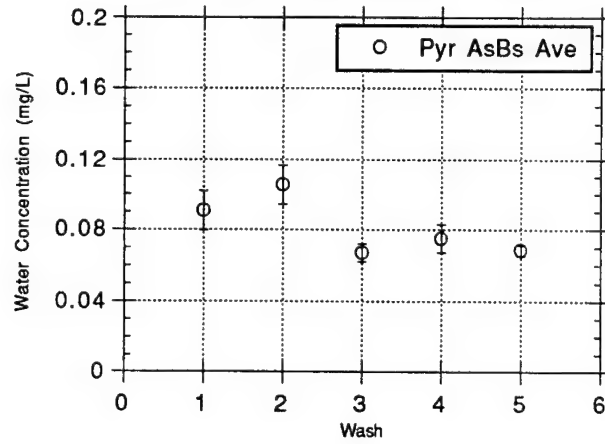
**Figure 5.5c: PT#4 Solution Concentrations
in Sequential Water Washes**



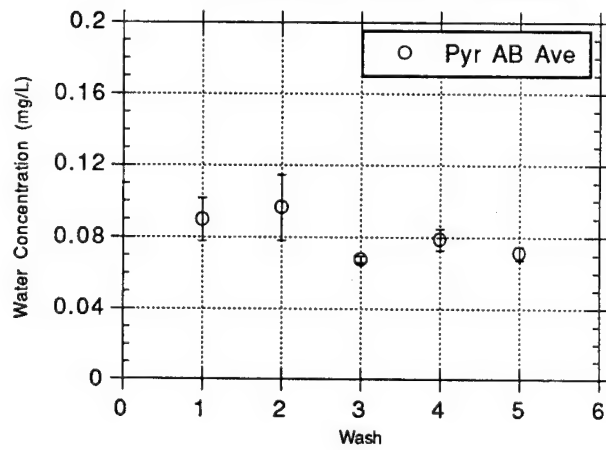
**Figure 5.6a: PT#4 Solution Concentrations
In Sequential Water Washes**



**Figure 5.6b: PT#4 Solution Concentrations
in Sequential Water Washes**



**Figure 5.6c: PT#4 Solution Concentrations
in Sequential Water Washes**



SOIL CONCENTRATIONS IN SEQUENTIAL WATER WASHES

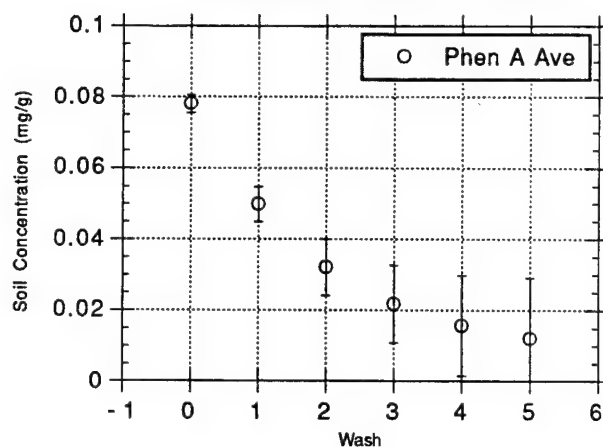
Calculated soil concentrations of phenanthrene and pyrene are shown in Figures 5.7a - 5.12c as a function of the number of 40 ml water washes for each of the three tests. The soil concentration was calculated from the mass of chemical removed by water washing. The mass at zero wash shows the initial measured soil concentration before washing.

The data show a progressive but slowing decrease in residual phenanthrene soil concentration in PT#2 for all three sand combinations (see Figures 5.7a,b,c). The lowest residual concentrations are approximately 0.01 mg/g. The PT#3 results on phenanthrene in Figures 5.9a,b,c show a similar trend. However, the PT#3 test data after five washes show residual masses that are somewhat higher with phenanthrene alone but lower with the two mixtures. The higher concentration is consistent with the fact that about twice as much chemical was present at the start of the test.

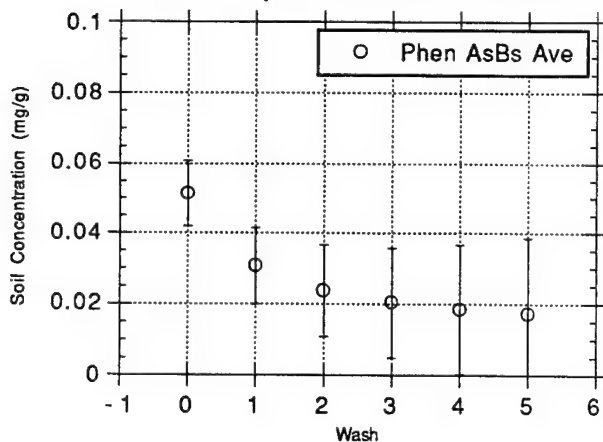
PT#4 test results which started with still higher initial phenanthrene concentrations (Figures 5.11a,b,c) also show progressive but slowing decreases in residual phenanthrene for all three sand combinations. The residual masses after 5 washings are significantly higher in all three soil mixtures compared with the PT#2 test.

The pyrene test results in Figures 5.8a,b,c; 5.10a,b,c; 5.12a,b,c are remarkably similar. Initial pyrene concentrations were the same in all three tests (PT#2,PT#3,PT#4) and residual soil concentrations decreased progressively but very slowly. The slow removal of pyrene is consistent with its low solubility.

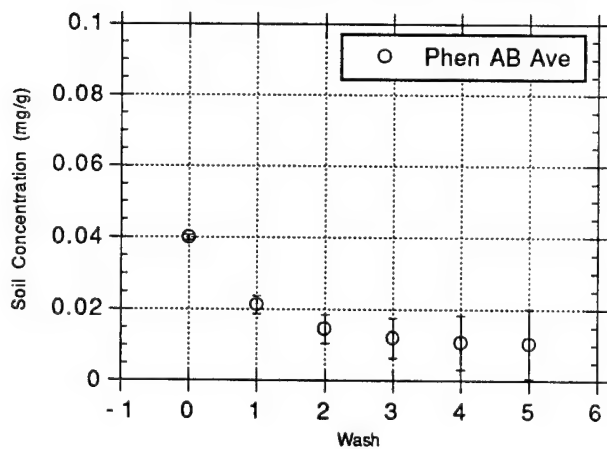
**Figure 5.7a: PT#2 Soil Concentrations
in Sequential Water Washes**



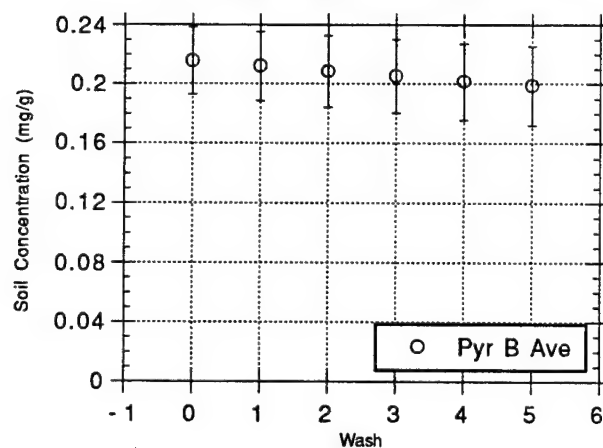
**Figure 5.7b: PT#2 Soil Concentrations
in Sequential Water Washes**



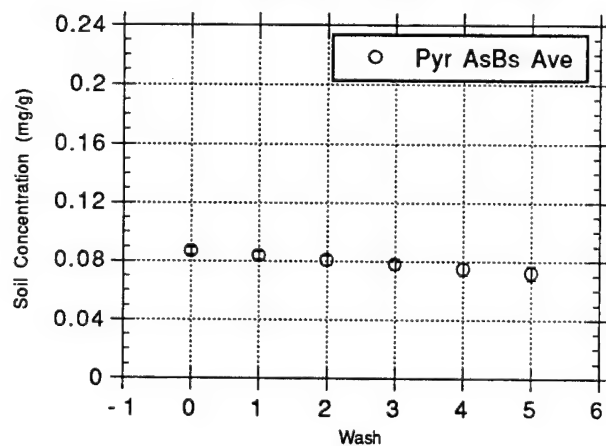
**Figure 5.7c: PT#2 Soil Concentrations
in Sequential Water Washes**



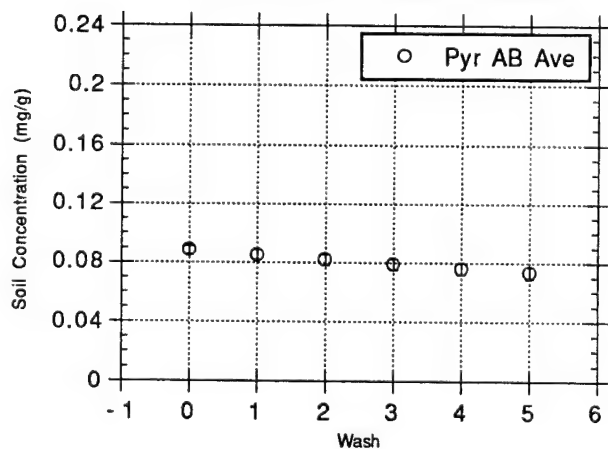
**Figure 5.8a: PT#2 Soil Concentrations
in Sequential Water Washes**



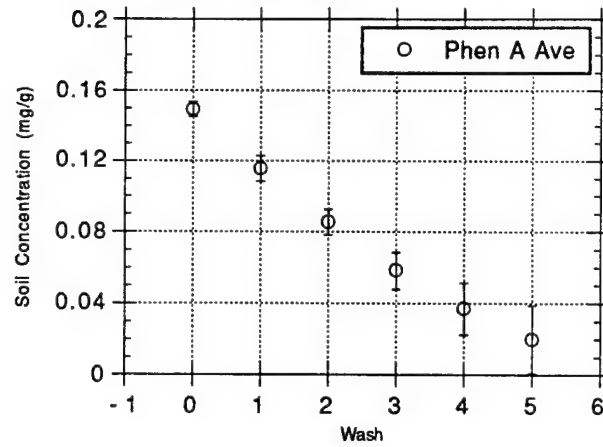
**Figure 5.8b: PT#2 Soil Concentrations
in Sequential Water Washes**



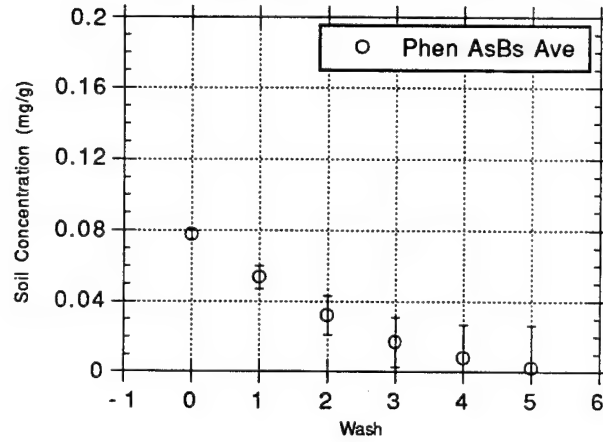
**Figure 5.8c: PT#2 Soil Concentrations
in Sequential Water Washes**



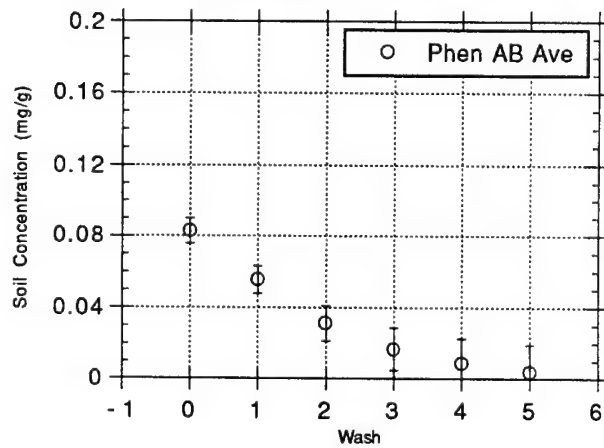
**Figure 5.9a: PT#3 Soil Concentrations
in Sequential Water Washes**



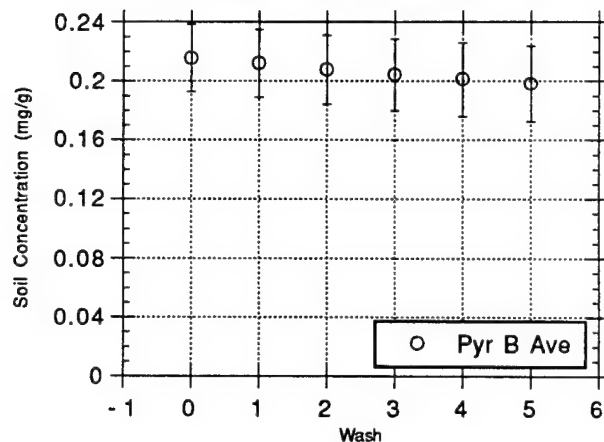
**Figure 5.9b: PT#3 Soil Concentrations
in Sequential Water Washes**



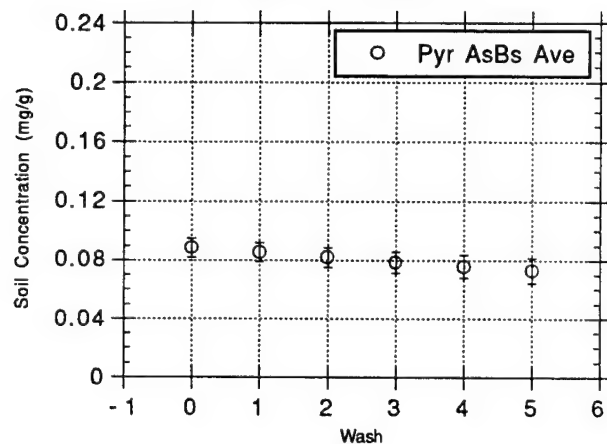
**Figure 5.9c: PT#3 Soil Concentrations
in Sequential Water Washes**



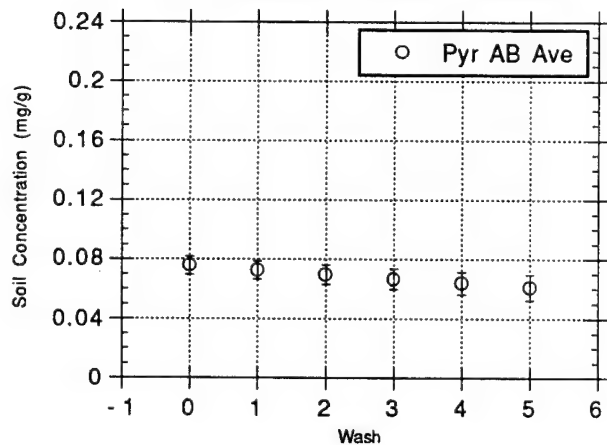
**Figure 5.10a: PT#3 Soil Concentrations
in Sequential Water Washes**



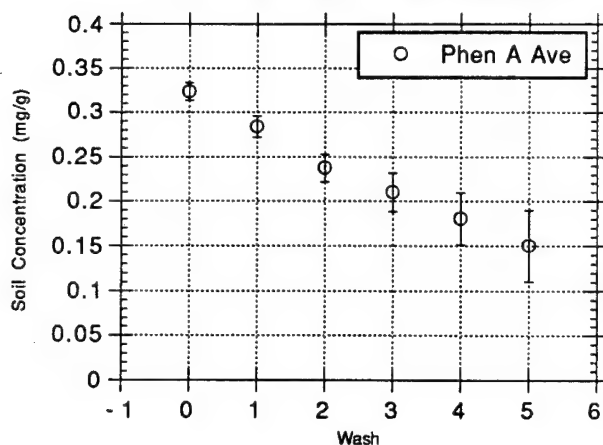
**Figure 5.10b: PT#3 Soil Concentrations
in Sequential Water Washes**



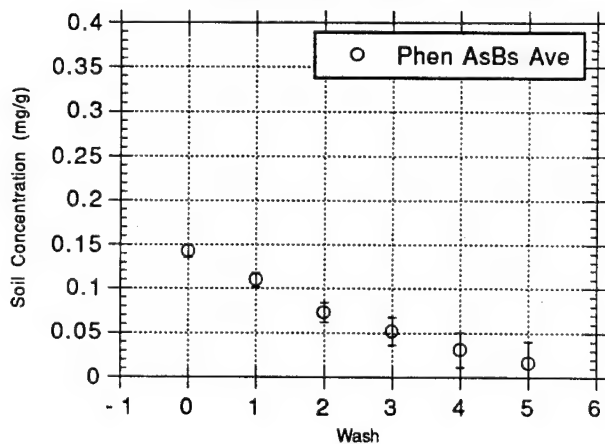
**Figure 5.10c: PT#3 Soil Concentrations
in Sequential Water Washes**



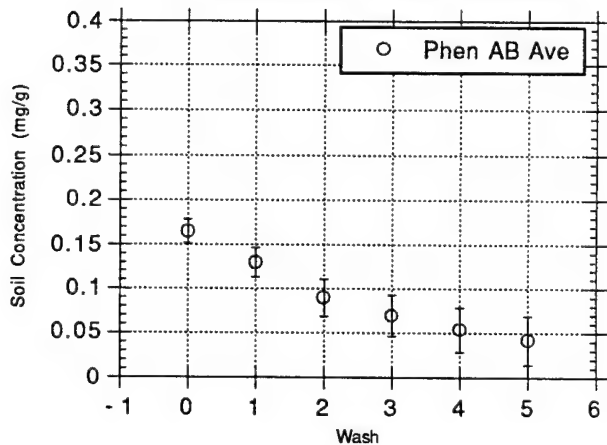
**Figure 5.11a: PT#4 Soil Concentrations
in Sequential Water Washes**



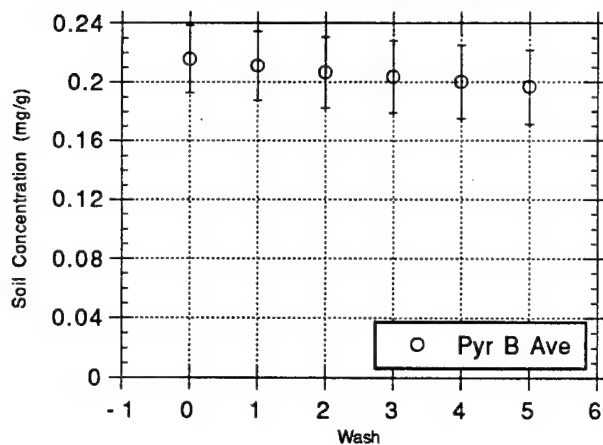
**Figure 5.11b: PT#4 Soil Concentrations
in Sequential Water Washes**



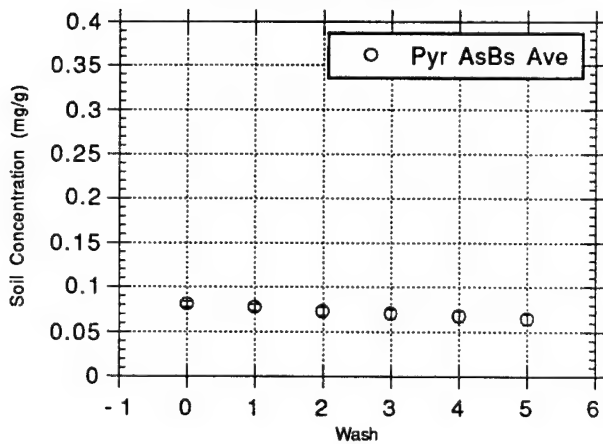
**Figure 5.11c: PT#4 Soil Concentrations
in Sequential Water Washes**



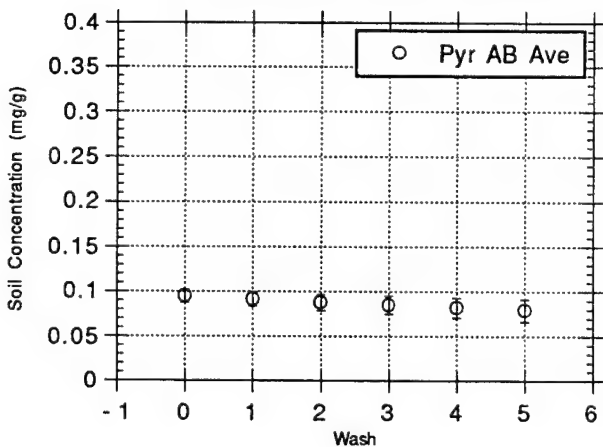
**Figure 5.12a: PT#4 Soil Concentrations
in Sequential Water Washes**



**Figure 5.12b: PT#4 Soil Concentrations
in Sequential Water Washes**



**Figure 5.12c: PT#4 Soil Concentrations
in Sequential Water Washes**



ANALYSIS OF WATER AND SOIL CONCENTRATION DATA

Measured water phase concentration (after four days of shaking) have been correlated with the calculated residual soil concentration data to examine whether solubilities correlate with residual soil concentrations. The results are shown in Figures 5.13a - 5.18c. Each water concentration data point represents the average of three measurements (three replicate tests were carried out at the same time). Y-axis error bars representing one standard deviation of the measured water concentrations are shown in each graph to give perspective on reproducibility of the data. Error bars for the X-axis were determined by including the standard deviation for the initial soil concentration as determined by the hexane extraction of the "dry" soils. Then since each subsequent soil concentration was determined by using the previous one, the standard deviations were added together, therefore reflecting both the error in the initial soil concentration and the water concentration measurements. That is why the error bars increase with decreasing soil concentration. One thing to note however is that if an error does exist for a point due to the initial soil concentration, this error will be consistent for all succeeding points. For example, if the concentration of chemical on the soil is estimated to be 0.005 mg/g too high to start with, each succeeding point will also be 0.005 mg/g too high. Therefore, an error in the initial soil concentration would merely shift the regression line to the right or to the left. It would not change its slope. Since there was good reproducibility with regards to water phase concentration measurements as demonstrated earlier, it is most likely that any error in these plots is the result of inaccurate initial soil concentration estimation.

Analysis of Phenanthrene Data

As shown in Figures 5.13a,b,c all three soil tests in PT#2 showed a quasi linear increase in water concentration with increasing soil concentration. Linear regressions gave good fits as indicated by correlation coefficients (R values) of 0.999, 0.98, and 0.999

respectively for soils with phenanthrene, mixtures of soils, and soil covered with the mixture. Correlation coefficients were calculated using the software package KaleidaGraph and are designated by "R" on each plot; a value of 1 represents a perfect linear fit. The corresponding R^2 values of 0.998, 0.961, and 0.998 indicate that regression accounts for most of the variance of water concentration.

However, it is important to note that the slopes were significantly different, the two mixtures were quite similar (36.9, 42.3) but were about twice the slope for phenanthrene alone (slope = 16.45). The implications of these differences are discussed in subsequent sections.

For PT#3 the phenanthrene showed very definite upward trends. The calculated linear regressions as shown in Figures 5.15a,b,c gave reasonably high values of R^2 = 0.958, 0.907, 0.890, indicating that there is a strong correlation. Again, the slopes for the two mixtures were very similar (9.11, 11.02) and about twice as large as the slope for the phenanthrene alone (slope = 4.27). However, all the slopes are significantly lower than the PT#2 test data. Furthermore, visual examination of the plots indicates that nonlinear fitting would probably give better fits. The implication of deviations from linearity is discussed in later sections.

Linear regression analysis of the PT#4 test results on phenanthrene also showed upward trends but gave lower correlation coefficients ($R = 0.66, 0.84, 0.85$) as shown in Figures 5.17a,b,c. Visual examination of Figure 5.17a shows that there is considerable scatter about the linear regression line. Furthermore, it does not appear that simple nonlinear regressions such as logarithmic or exponential correlations would explain the high values of the 4th data point in each set. The calculated slopes for the three soil samples (2.59, 5.08, 7.52) are also significantly lower than those from the PT#2 and PT#3 test. Just as observed in the other two tests, the slopes of the two mixtures were quite similar (5.08, 7.52) but are about twice that of the phenanthrene alone (slope = 2.59).

Analysis of Pyrene Data

The corresponding graphs for pyrene (Figures 5.14a,b,c for PT#2) showed slight upward trends (slopes = 1.21, 0.684, 1.01) but considerable data scatter. The correlation coefficients (R) were relatively low as shown in the figure. The corresponding R^2 values of 0.567, 0.248, 0.778 indicate that the regression is weak because it explains a relatively small part of the variance. This could be due to the narrow range of measured water phase concentrations which relate to the fact that pyrene is very slightly soluble. As a result, the small changes in soil concentrations during the five washes were very small.

Pyrene test results from PT#3 and PT#4 showed very similar trends to those observed in PT#2. This is not surprising because the same initial soil concentrations were used in all three tests. Water concentrations showed very slight upward trends but there was considerable scatter of the data around the linear regression lines as shown in figures 5.16a,b,c and 5.18a,b,c. This may in part be due to the narrow range of measured values for both the water and soil concentrations. The error bars on each of the 5 points actually overlap the whole range of test concentrations. The slopes from the three tests are compared below.

Slopes of Correlation lines

	PyB	Py AsBs	PyAB
PT#2	1.21	0.68	1.01
PT#3	1.72	0.91	0.60
PT#4	2.19	2.30	1.70

The slopes of all the correlation lines are low. One possible explanation for the low slopes is that the soil concentrations did not change much because of the low solubility of pyrene. In view of the fact that the same initial pyrene concentrations were used in all three tests it is not surprising to find comparable slopes between the three tests. In

retrospect it would have been helpful if some of the tests had been carried out for longer times to measure the changes in water phase concentrations at lower soil concentrations.

In summary, test data on phenanthrene clearly show that water phase concentrations are correlated with soil concentrations at low soil concentrations but approach saturation at higher soil concentrations. The sequential washing test data using three levels of initial phenanthrene concentrations show that :

- (a) Lower solubilities are obtained as soil concentrations decrease.
- (b) Individual test results show strong linear correlations over the relatively narrow range of soil concentrations that were observed in each test.
- (c) Regression slopes are progressively lower with increasing initial phenanthrene concentrations, $PT\#2 > PT\#3 > PT\#4$. They would be expected to approach zero at high soil concentrations where saturation concentrations are obtained.
- (d) It therefore appears that the linear correlations represent piecewise correlations of the changes in water phase concentrations for relatively narrow ranges in soil concentrations. The implication is that a nonlinear model that incorporates the concept of an asymptotic approach to saturation concentration would be more appropriate. This concept is examined in the following sections.

One possible explanation for the lower solubility at low soil concentrations is that there is some chemical bonding to the mineral surfaces. The energy required to solubilize phenanthrene that is present as a solid phenanthrene phase is probably smaller than the energy needed when phenanthrene is bound to the mineral surfaces in the form of a thin film. The question of how this compares with the energy required for solubilizing adsorbed species is unclear and probably depends on whether the adsorbed chemicals are solids or quasi solutions on the soil surfaces.

Figure 5.13a: PT#2 Water Concentration Vs Soil Concentration

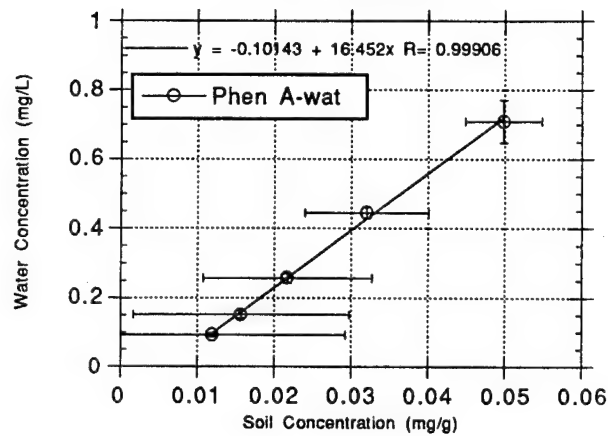


Figure 5.13b: PT#2 Water Concentration Vs Soil Concentration

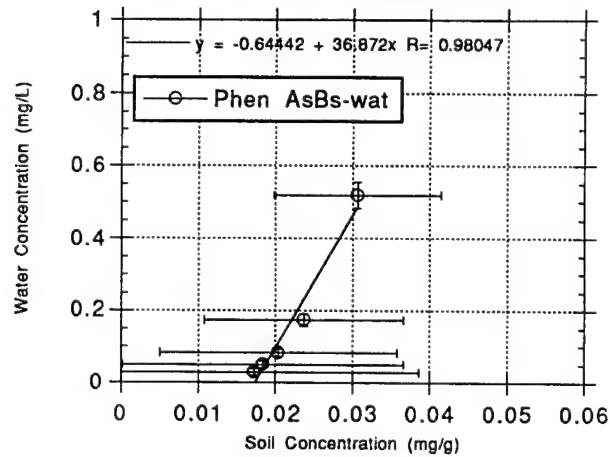


Figure 5.13c: PT#2 Water Concentration Vs Soil Concentration

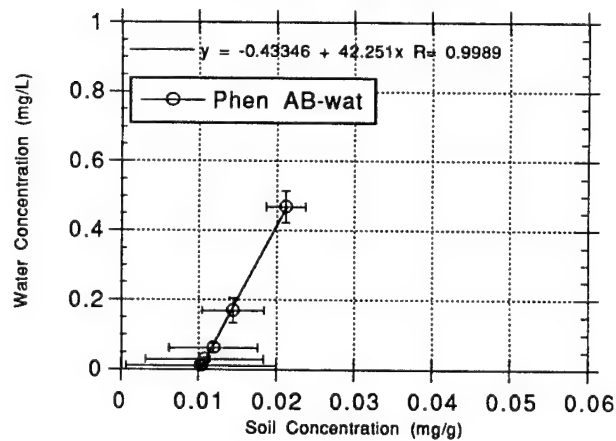


Figure 5.14a: PT#2 Water Concentration
Vs Soil Concentration

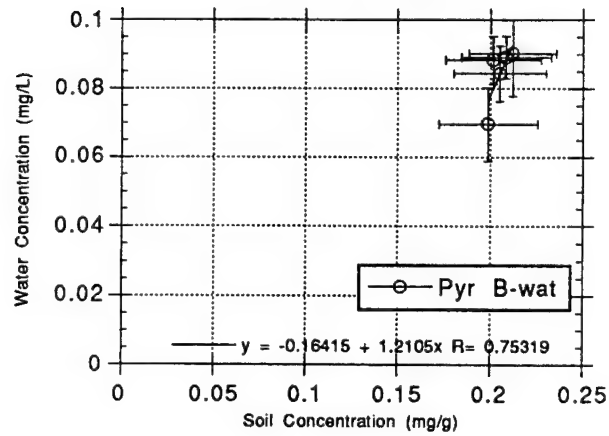


Figure 5.14b: PT#2 Water Concentration
Vs Soil Concentration

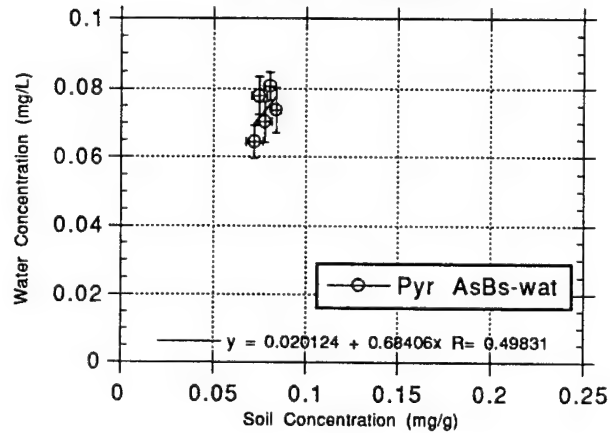


Figure 5.14c: PT#2 Water Concentration
Vs Soil Concentration

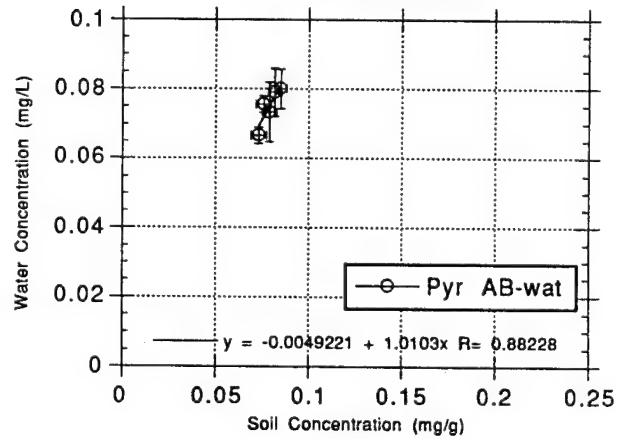


Figure 5.15a: PT#3 Water Concentration
Vs Soil Concentration

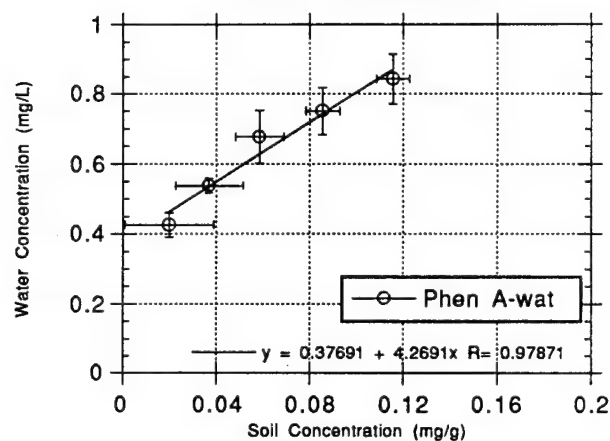


Figure 5.15b: PT#3 Water Concentration
Vs Soil Concentration

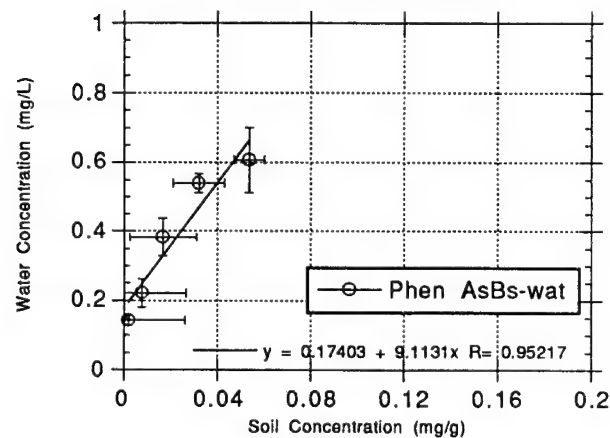


Figure 5.15c: PT#3 Water Concentration
Vs Soil Concentration

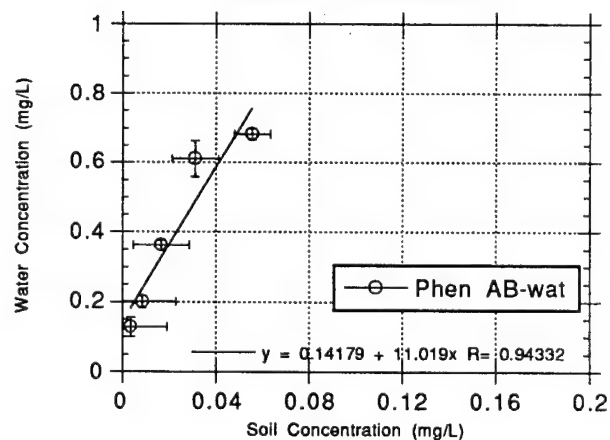


Figure 5.16a: PT#3 Water Concentration
Vs Soil Concentration

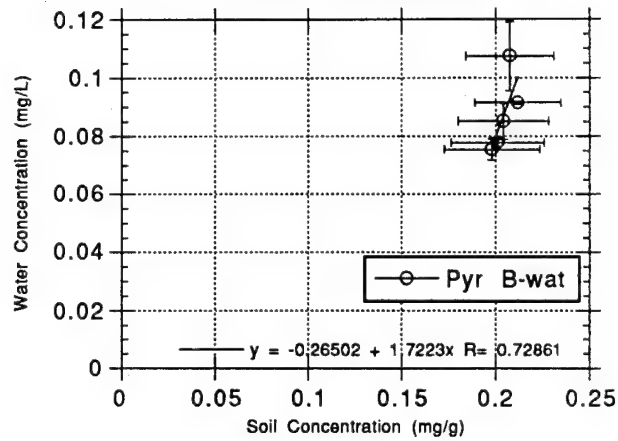


Figure 5.16b: PT#3 Water Concentration
Vs Soil Concentration

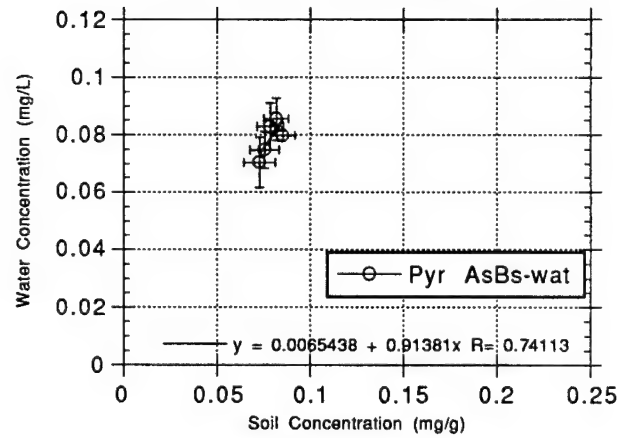


Figure 5.16c: PT#3 Water Concentration
Vs Soil Concentration

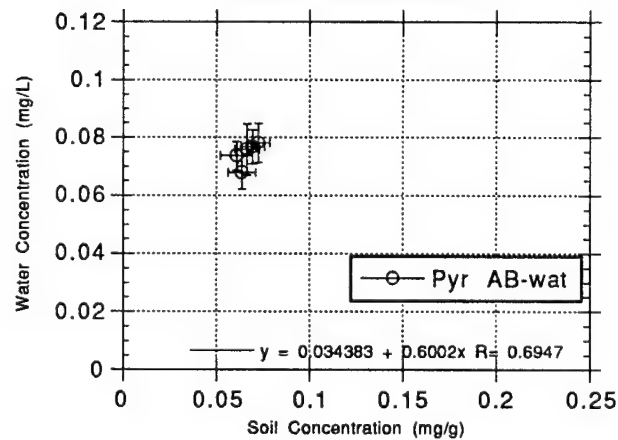


Figure 5.17a: PT#4 Water Concentration
Vs Soil Concentration

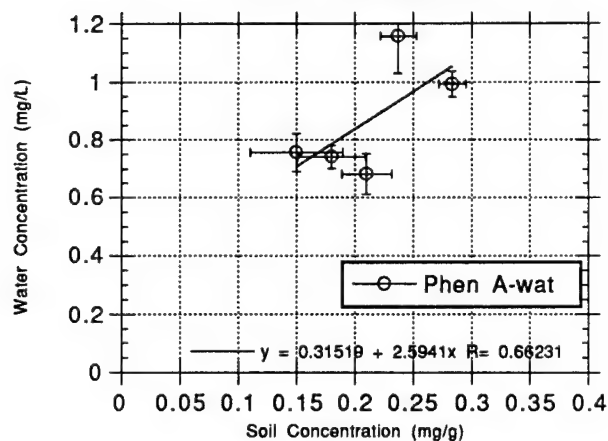


Figure 5.17b: PT#4 Water Concentration
Vs Soil Concentration

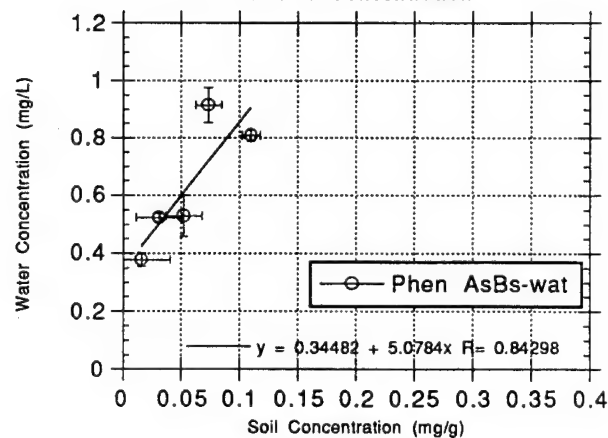
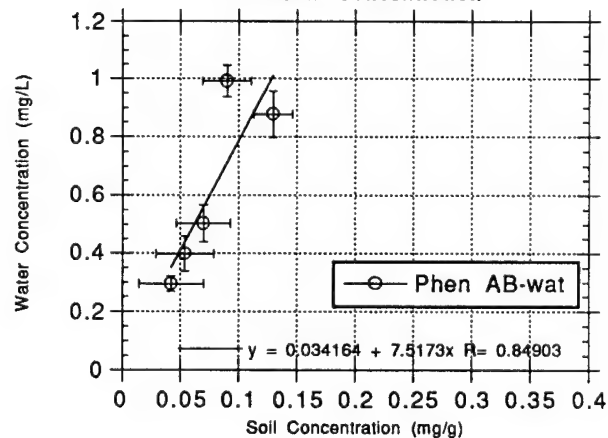
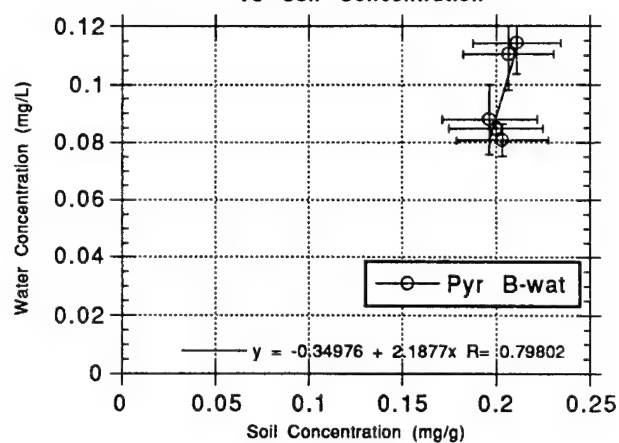


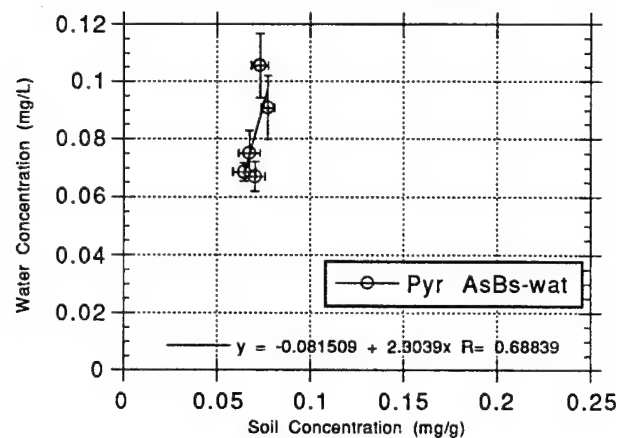
Figure 5.17c: PT#4 Water Concentration
Vs Soil Concentration



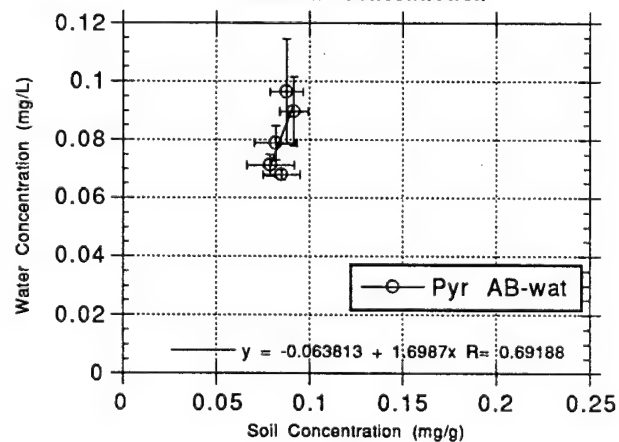
**Figure 5.18a: PT#4 Water Concentration
Vs Soil Concentration**



**Figure 5.18b: PT#4 Water Concentration
Vs Soil Concentration**



**Figure 5.18c: PT#4 Water Concentration
Vs Soil Concentration**



DISCUSSION OF COMBINED DATA SETS

Analysis of the combined data sets is presented in the form of answers to three questions.

a) Is dissolution of a chemical from a soil dependent upon the amount of chemical remaining on the soil?

Water and Soil Concentration data from all three tests were pooled and plotted together for pure phenanthrene and pure pyrene. In both cases the upper graph identifies the data sets and show how they fit together. The lower graph does not differentiate between the data sets but makes it easier to see the trends.

Analysis of Phenanthrene Data

When plots were made of soil concentration vs water concentration as previously discussed, there was a definite trend for soils with low initial concentrations of phenanthrene (<0.15 mg/g or so). Less distinct trends were observed on soils with higher initial concentrations. This is made even clearer in the combined plots as shown in Figures 5.19a and b. There is an initial steep curve that levels off as it nears the expected saturation concentration of the phenanthrene (about 0.8 to 0.9 mg/L). This shows that at lower soil concentrations the phenanthrene is less soluble and therefore its solubility is dependent on soil concentration. It also seems to imply that there is a soil concentration at which the water phase chemical concentration in equilibrium with it reaches saturation concentration and therefore beyond this point water concentration is independent of soil concentration.

It can be clearly seen in both Figure 5.19a and b that the second to last phenanthrene point is at a water concentration that is considerably higher than what is expected based on previous results as well as the current trend. This same phenomena was mentioned earlier in the section discussing the plots of "Soil Concentrations in Sequential Water Washes". It was mentioned that this could be due to an extra day of equilibration or even a faulty GC calibration. The fact that this point is consistently high for all data taken on that day would support either one of these conclusions.

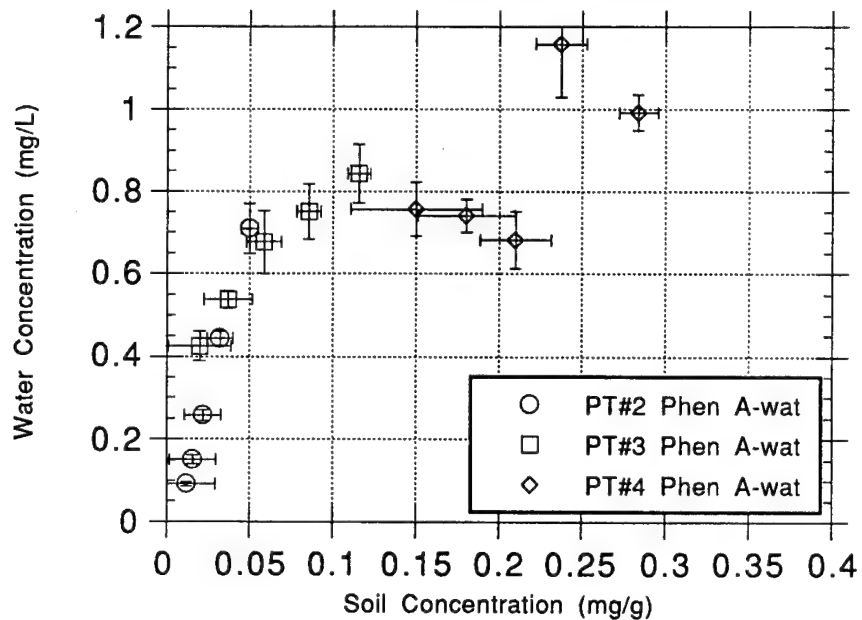
Analysis of Pyrene Data

The same type of plot with pyrene yielded a shallow upward trend with a considerable amount of scatter as seen in Figure 5.20a. Since the pyrene coated sand remained at a higher soil concentration due to its low solubility, this is consistent with the phenanthrene results in that a more shallow slope is observed at higher soil concentrations.

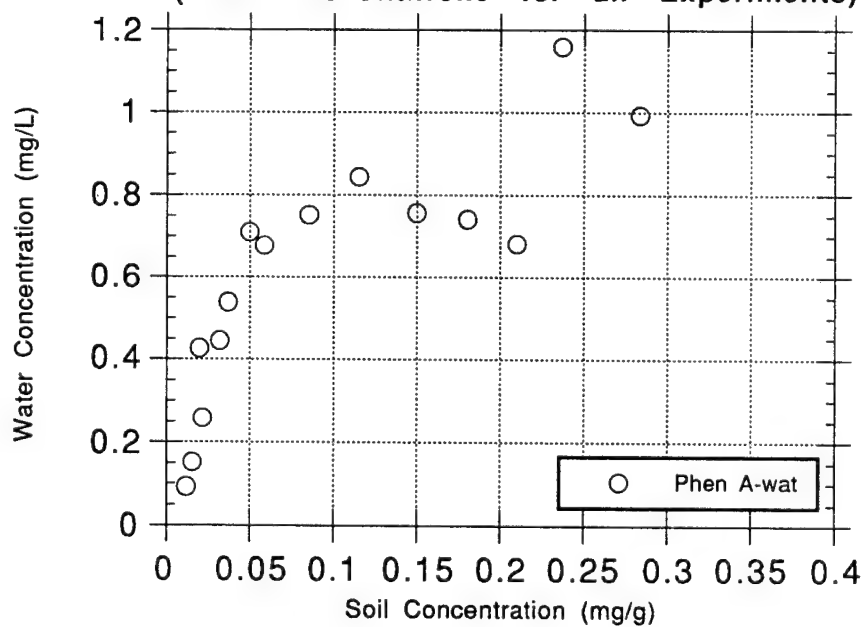
Our theory is that at high chemical concentrations on the soil, the chemical coats the entire sand grain surfaces and therefore any chemical that dissolves requires sufficient energy to break the bonds holding it to like molecules. This includes the energy of the state change from solid into the liquid phase. This situation is very similar to having excess chemical shaking in water, one expects to see something close to saturation concentrations. Therefore, at levels greater than approximately 0.15mg/g, the solution concentration is essentially independent of sand concentration provided that there is sufficient time for equilibration. This same effect is hidden in the pyrene data because concentrations on the soil never got below this level, there was only a very slight overall decrease in solution concentration with decrease in mass on soil.

On the other hand, for the lower levels of phenanthrene there was a definite drop in solution concentration with decreasing soil concentration. The explanation is that at lower soil concentrations, it is more limited because progressively more molecules are bound to the mineral surface itself instead of to other like molecules. We infer that these bonds require more energy to overcome them than do the others as indicated by the lower dissolution rates. It is possible that these observation are related to the method by which the chemical is impregnated on the soil. In these studies dry soil was coated with hexane solubilized phenanthrene and pyrene. It was designed to mimic the introduction of slightly soluble PAH in creosote into subsurface environments followed by weathering of the light ends. The effects of soil type and surface area were not evaluated in this study, nor were other solvents tested.

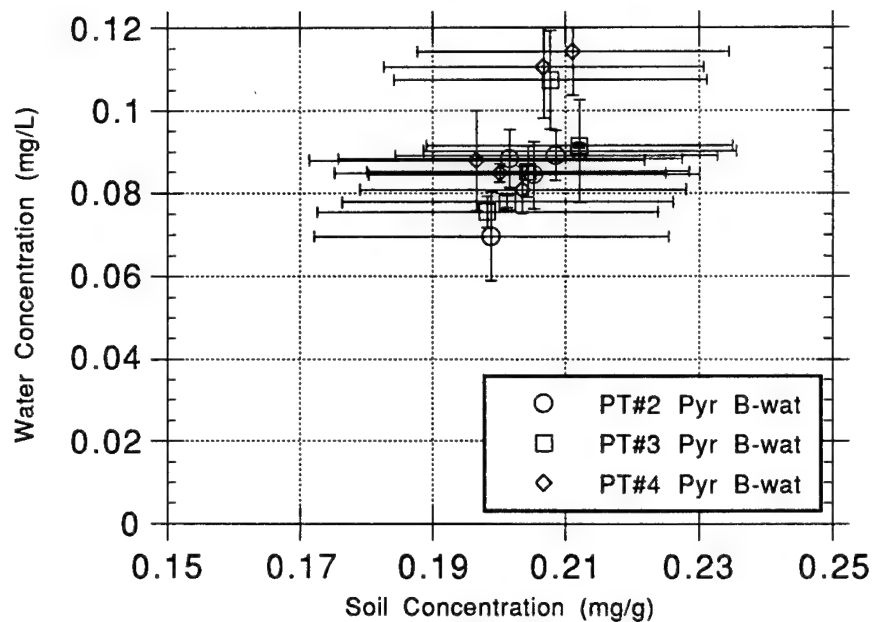
**Figure 5.19a: Water Concentration
Vs Soil Concentration
(Pure Phenanthrene)**



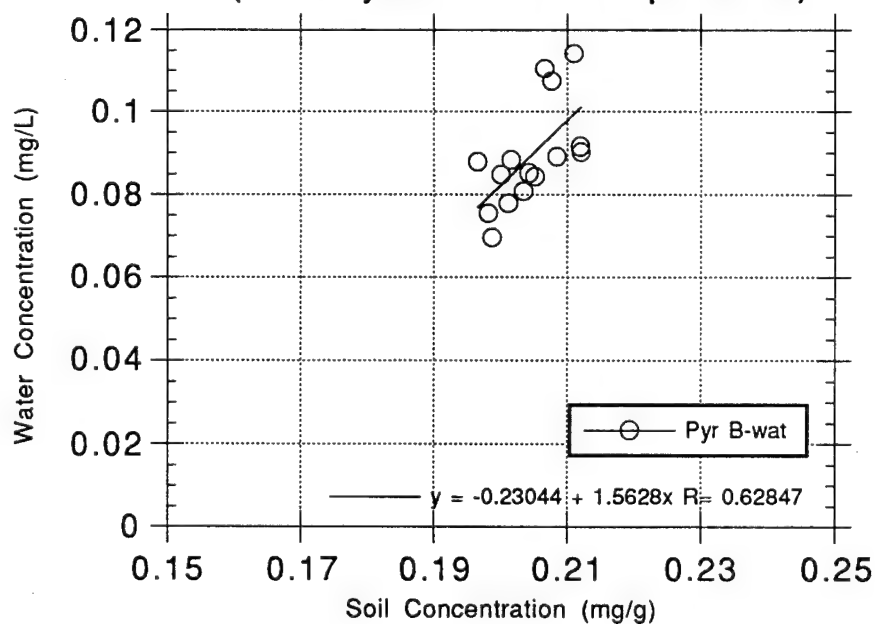
**Figure 5.19b: Water Concentration
Vs Soil Concentration
(Pure Phenanthrene for all Experiments)**



**Figure 5.20a: Water Concentration
Vs Soil Concentration
(Pure Pyrene)**



**Figure 5.20b: Water Concentration
Vs Soil Concentration
(Pure Pyrene for all Experiments)**



b) How does the presence of mixtures of chemicals affect their dissolution in comparison to pure compounds?

“Water Concentration Vs Soil Concentration” plots were made pooling together the pure phenanthrene data from PT#2 and the phenanthrene mixture data from PT#3 (see Figure 5.21a). The same was done for the pure phenanthrene data from PT#3 and the phenanthrene mixture data from PT#4 (see Figure 5.21b). This was done because the initial phenanthrene concentrations in all three systems for each set was essentially the same. This made it possible to look at the effect of being in a mixture on the dissolution of phenanthrene.

First of all, the pure phenanthrene trial from PT#2 (initial phenanthrene soil concentration = 0.0782 mg/g) was compared to the mixtures for PT#3 (initial phenanthrene soil concentration = 0.078 mg/g (AsBs), 0.083 (AB); initial pyrene concentration = 0.0886 (AsBs), 0.0758 (AB)). “Water Concentration Vs Soil Concentration” plots were constructed for all of them. They all yielded fairly linear relationships ($R^2_A = 0.998$, $R^2_{AsBs} = 0.907$, $R^2_{AB} = 0.890$) but the slope of the pure phenanthrene was somewhat higher than the slope of the mixtures ($slope_A = 16.46$, $slope_{AsBs} = 9.11$, $slope_{AB} = 11.02$). This would support the notion that the dissolution of one PAH from the soil is affected by the presence of a second.

A two-sample hypothesis t-test of the mean was conducted on the slopes of the lines at the 5% significance level and it could be concluded with 99.27% certainty that the slope of the phenanthrene alone would not be equal to the slope of the AsBs mixture (Kiemele and Schmidt, 1991). The same test was also conducted on the AB mixture regression line and it could be concluded with 99.34% certainty that it was not equal to the pure phenanthrene slope. These tests support that the difference in dissolution observed between the pure phenanthrene and a mixture of phenanthrene (no matter the method of application) are significant.

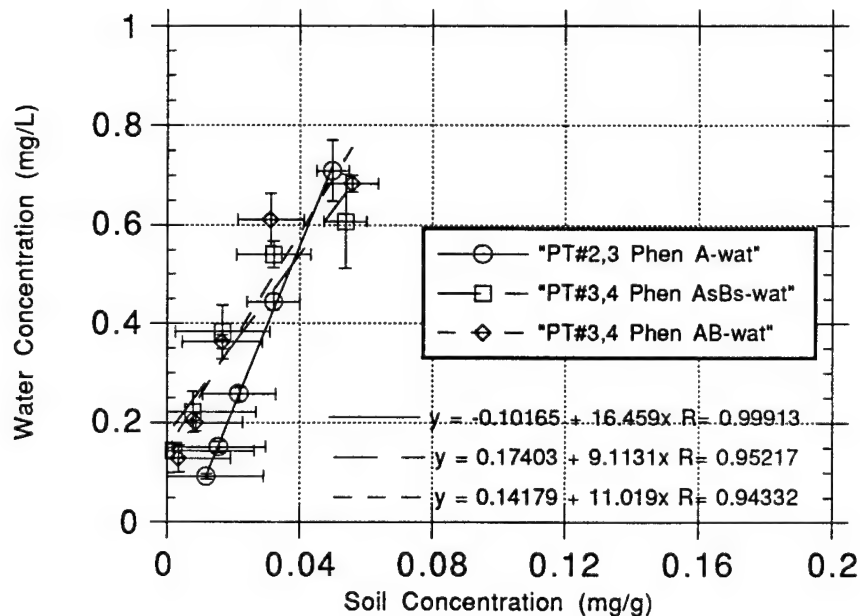
Next the pure phenanthrene trial from PT#3 (initial phenanthrene soil concentration = 0.1493 mg/g) was compared to the mixtures for PT#4 (initial phenanthrene soil concentration = 0.1423 mg/g (AsBs), 0.1647 (AB); initial pyrene concentration = 0.0811 (AsBs), 0.0953 (AB)). "Water Concentration Vs Soil Concentration" plots were constructed for all of them. They all yielded fairly linear relationships ($R^2_A = 0.958$, $R^2_{AsBs} = 0.711$, $R^2_{AB} = 0.721$) but the slope of the pure phenanthrene was somewhat lower than the mixtures this time ($slope_A = 4.27$, $slope_{AsBs} = 5.08$, $slope_{AB} = 7.51$).

A two-sample hypothesis t-test of the mean was again conducted on the slopes of the lines at the 5% significance level (Kiemele and Schmidt, 1991). It could not be concluded that the difference in the phenanthrene slopes was significant at this level for the pure phenanthrene and the AsBs mixture. Another t-test was done on this same set of data minus the second sample which was questionable due to its disagreement with the other points, and the same conclusion was arrived at. The same two tests were also conducted on the AB mixture regression line. In the first one which included the questionable data, it was concluded with 96.52% certainty that it was not equal to the pure phenanthrene slope. The second however failed to conclude this within the required significance level. Due to the nature of the data as well as the low percent certainty for the initial calculation, it seems probable that the second conclusion is more reliable. Assuming that this is indeed the case, these tests show that the difference in dissolution observed between the pure phenanthrene and a mixture of phenanthrene (no matter the method of application) are not statistically significant at this level.

When both sets of data were combined and fit with linear regressions in Figure 5.21c, the regression lines looked very similar and yielded very similar slopes (6.81, 6.44, 6.12). Similarly, when both sets of data were combined and fit with a log fit in Figure 5.21d, the two mixtures looked quite similar and although the phenanthrene fit looked somewhat different, it still resembled the other two a great deal. Analyzing the data in this

manner makes any differences look rather insignificant. Therefore the differences observed between the dissolution of a chemical applied as a mixture or as a pure compound seem to be more significant at low concentrations than at high concentrations and more pronounced over short soil concentration ranges than larger ones. This would be consistent with literature which supports the notion that for mixtures of solids that do not liquefy upon mixing, the solubility of the solid in water should be relatively unaffected by the presence of other solid components (Sugatt et al., 1984).

**Figure 5.21a: Water Concentration
Vs Soil Concentration
(Equal Initial Phenanthrene Masses)**



**Figure 5.21b: Water Concentration
Vs Soil Concentration
(Equal Initial Phenanthrene Masses)**

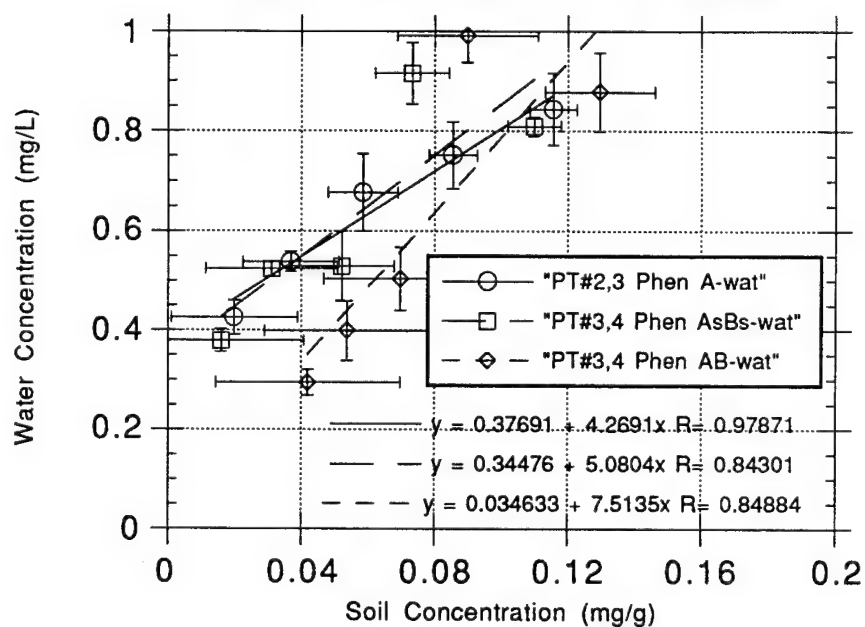


Figure 5.21c: Figure 5.21a and
Figure 5.21b Combined

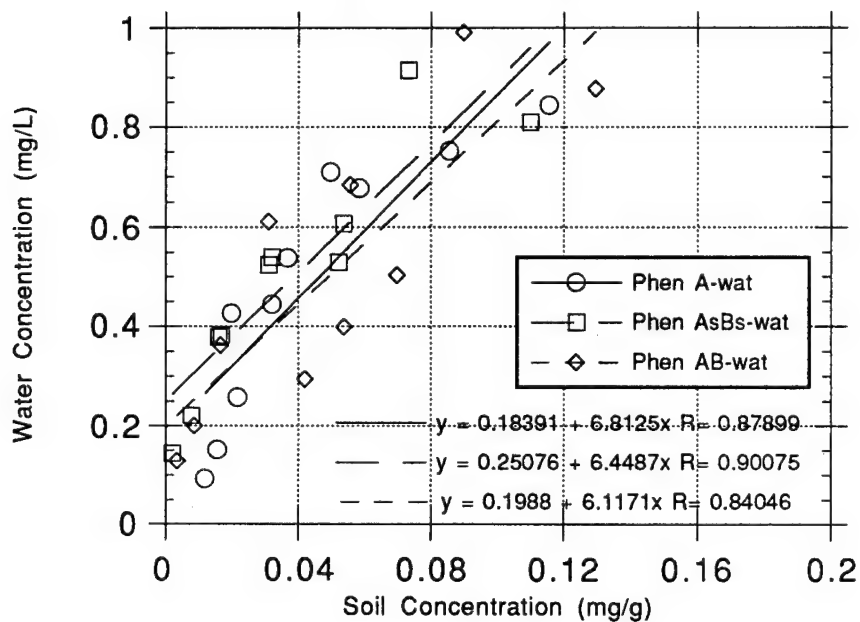
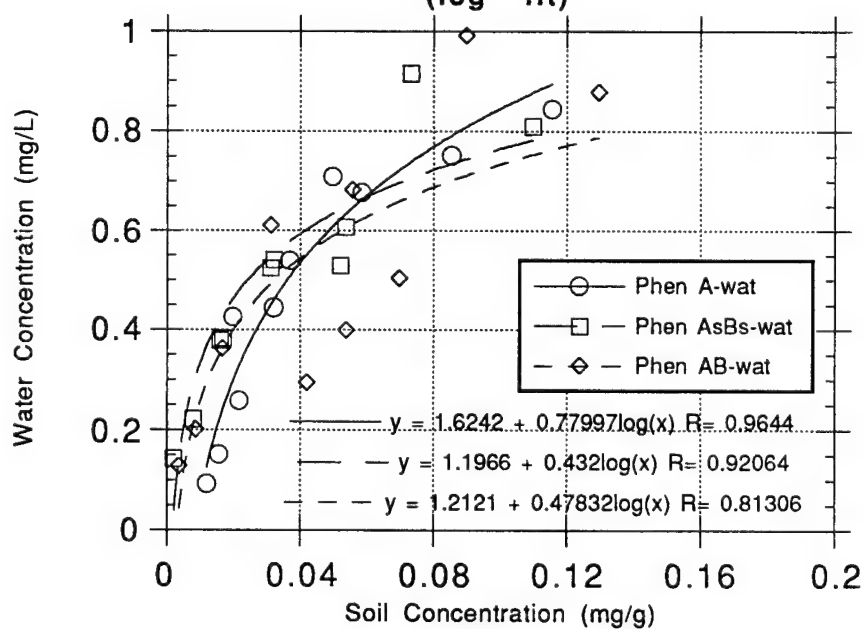


Figure 5.21d: Figure 5.21a and
Figure 5.21b Combined
(log fit)



c) Is there a difference between the dissolution of chemicals from soils coated with mixtures of chemicals and mixtures of soils each coated with individual chemicals?

Before performing these experiments, it was hypothesized that the dissolution of a higher soluble PAH (phenanthrene) would be hindered by the presence of a lower solubility PAH (pyrene) when the two were coated together. This was based on the idea that the phenanthrene would get hidden under layers of pyrene which would inhibit its dissolution due to its inability to make contact with the solvent (water).

Plots were made comparing the dissolution of the two mixture methods, each with the same mass concentration of chemicals. AsBs represents the mixing of phenanthrene coated soil with pyrene coated soil while AB represents soil coated with a solution of phenanthrene and pyrene dissolved in solvent together.

When plots were made comparing the dissolution of the same chemical masses coated on the sands as both mixtures (AB) and pure compounds (AsBs), little difference in concentration was observed in the water in equilibrium with the soil (see Figures 5.22a - 5.24b). This was tested by conducting a two-sample hypothesis t-test of the mean on the slopes of the lines at the 5% significance level for all three experiments (Kiemele and Schmidt, 1991).

Analysis of Phenanthrene Data

First we looked at phenanthrene and in all three experiments it was found that we could not conclude that the slopes were different to the significance level stated (see Figures 5.22a,b,c). One can see by looking at the plots that the regression lines are very similar so this conclusion seems reasonable. This would imply that the aqueous concentration of the chemical is independent of the method of coating the sand and is merely dependent on the mass present. In Figure 5.24a one can see that when the data from all three experiments are combined and plotted together, the regression lines that result for the two different mixtures are very similar supporting the notion that there is no significant difference in dissolution.

Analysis of Pyrene Data

The pyrene results were tested in the same manner and in all cases it was determined that the differences observed in dissolution between the two methods of coating were not significant based on the criteria chosen (see Figures 5.23a,b,c). It is also interesting to note that even though there is considerable scatter in this data, when all three tests are combined as with the phenanthrene, the regression lines that result for the two mixtures as seen in Figure 5.24b are almost exact even though their correlation coefficients are very low.

Therefore our data does not support the idea that the method of mixture application plays an important role in the dissolution of chemicals from soils for either the phenanthrene or the pyrene.

Figure 5.22a: PT#2 Water Concentration
Vs Soil Concentration
(Equal Chemical Masses Applied Differently)

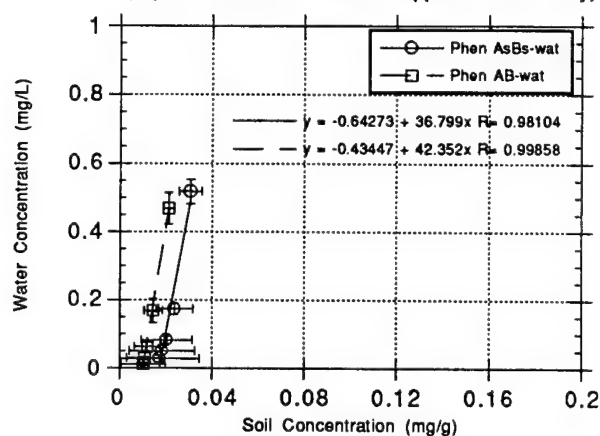


Figure 5.22b: Water Concentration
Vs Soil Concentration
(Equal Chemical Masses Applied Differently)

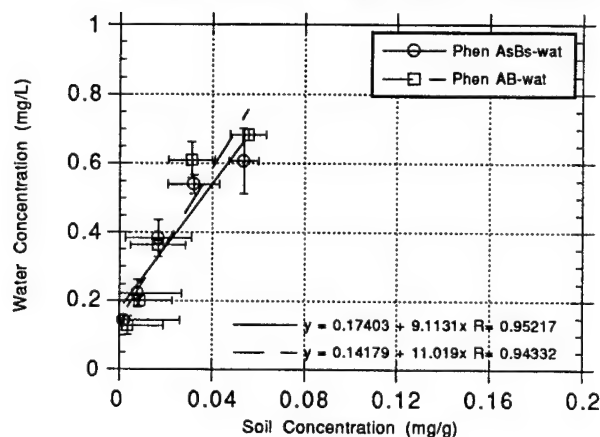


Figure 5.22c: PT#4 Water Concentration
Vs Soil Concentration
(Equal Chemical Masses Applied Differently)

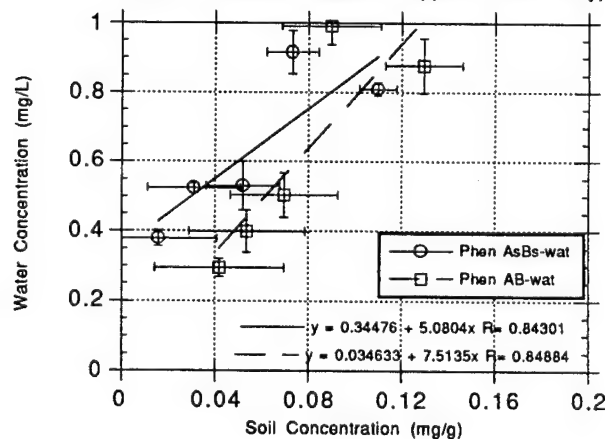


Figure 5.23a: PT#2 Water Concentration
Vs Soil Concentration
(Equal Chemical Masses Applied Differently)

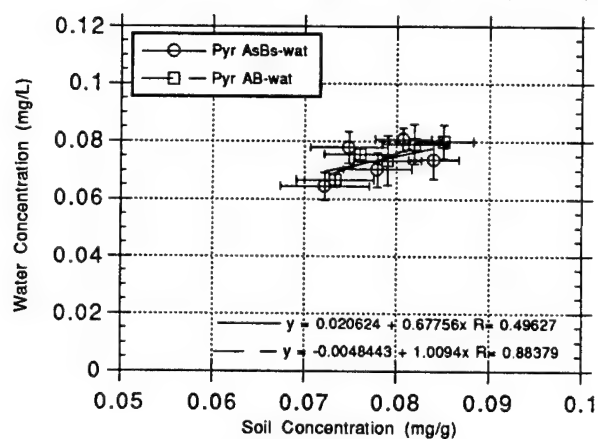


Figure 5.23b: PT#3 Water Concentration
Vs Soil Concentration
(Equal Chemical Masses Applied Differently)

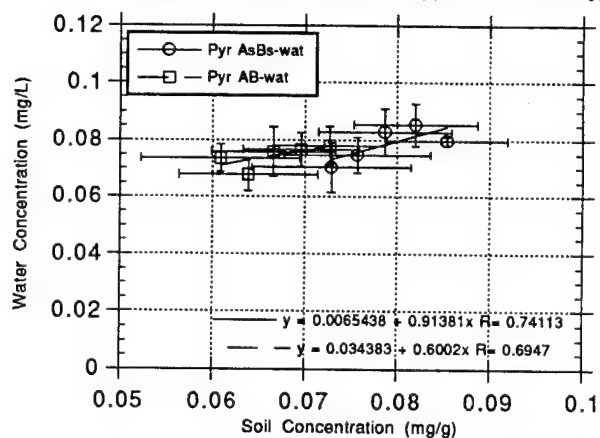
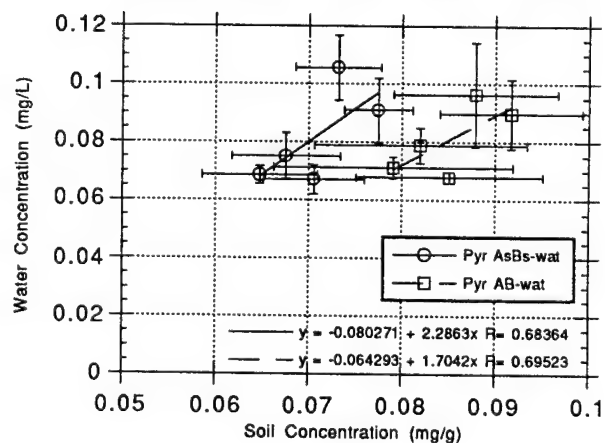
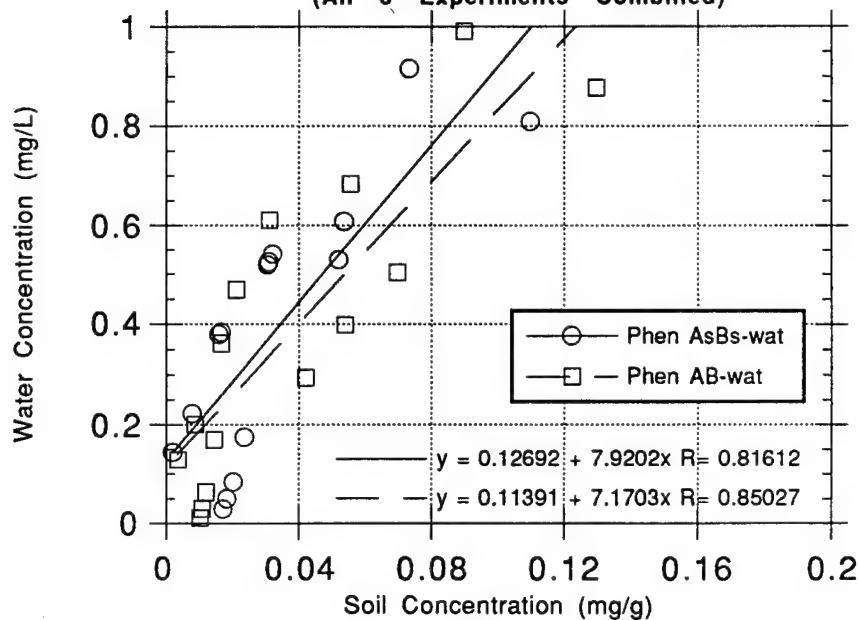


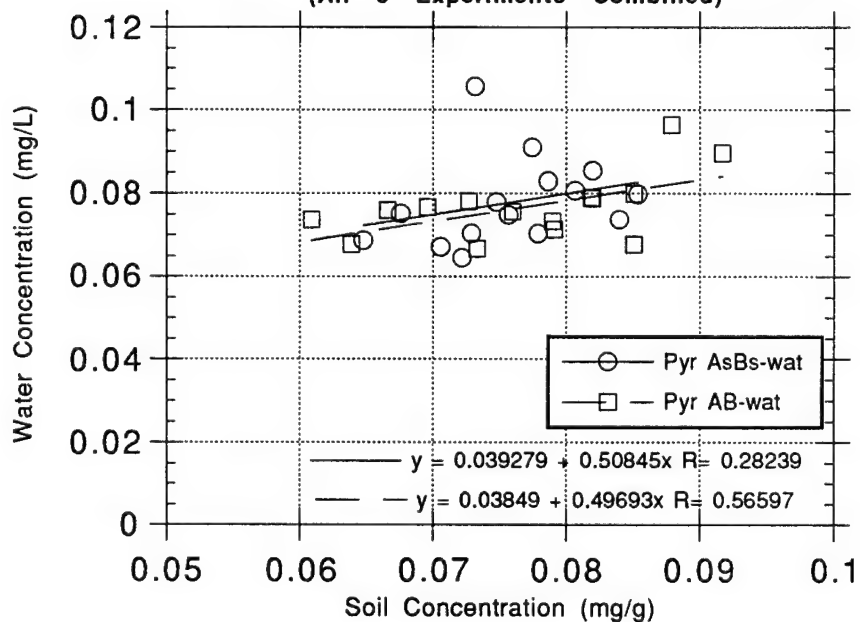
Figure 5.23c: PT#4 Water Concentration
Vs Soil Concentration
(Equal Chemical Masses Applied Differently)



**Figure 5.24a: Water Concentration
Vs Soil Concentration
(Equal Chemical Masses Applied Differently)
(All 3 Experiments Combined)**



**Figure 5.24b: Water Concentration
Vs Soil Concentration
(Equal Chemical Masses Applied Differently)
(All 3 Experiments Combined)**



COMPARISON TO DESORPTION STUDY

An interesting comparison was made between the correlations of phenanthrene coated sand and the adsorption desorption data from another study in our laboratory. The pure phenanthrene data from PT#2 were replotted to correlate soil concentration versus water concentration as is the practice in adsorption studies. These correlations were compared to Smit's (1995) desorption isotherm for phenanthrene from pure Jordan sand. Smit's data was found to produce a more shallow slope (0.0014 compared to 0.0607) and a lower intercept (0.001 compared to 0.006 mg/g). His desorption regression equation was used to generate data in order to plot his regression line on the same plot as the PT#2 data (see Figure 5.25a). Smit's desorption curve was also plotted alone in Figure 5.25b in order to make it easier to see. It is clear from these plots that the two sets of data represent two different types of physical phenomena. Such results would suggest that we are looking at a bond considerably stronger than that of adsorption.

Figure 5.25a: Comparison of Dissolution and Desorption Data

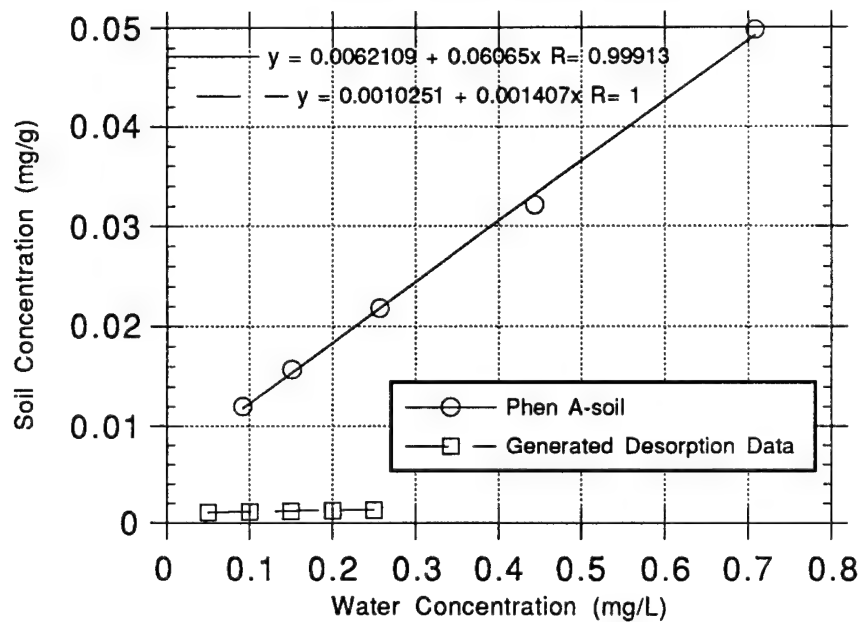
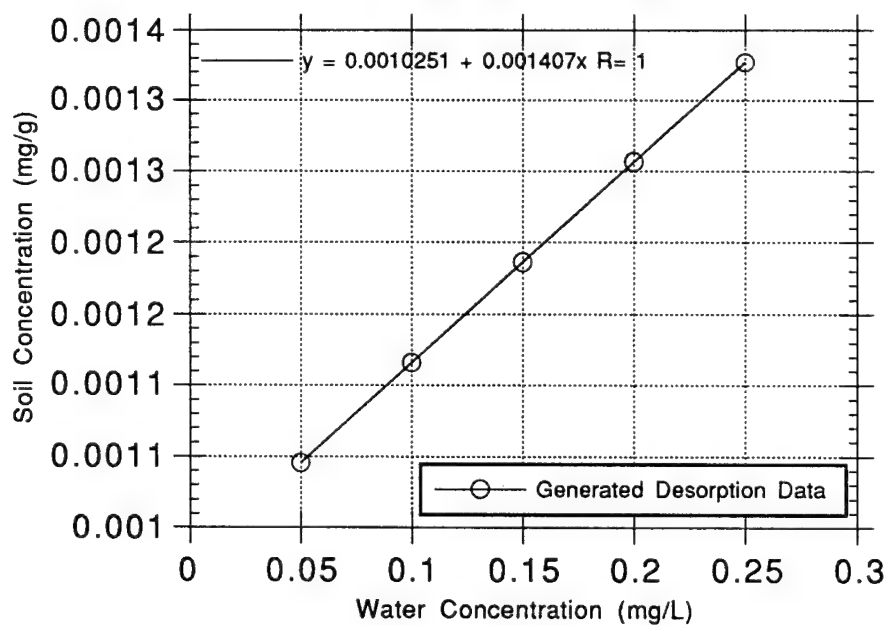


Figure 5.25b: Close-up of Generated Desorption Curve



OVERALL MASS BALANCE

Overall mass balances were calculated for each chemical as described in the methods section. Summaries of the calculations are shown in Tables 5.1 - 5.3. for all three experiments. In each case, A represents phenanthrene alone, B represents pyrene alone, AsBs represents phenanthrene coated soil mixed with pyrene coated soil, and AB represents soil coated with a mixture of phenanthrene and pyrene.

The total mass washed off the soil after five washes was determined by summing the amount of chemical as determined by the aqueous concentration. The mass extracted from the "dry" soil is the amount of chemical measured by hexane extraction of the coated soil. The mass extracted from "wet" soil is the amount recovered from the soils using hexane after the five water washes. The calculated mass left represents the amount of chemical expected to remain on the soil after the five washes. Mass of chemical remaining on the soil was also calculated using the initial mass as determined by the extraction of the "dry" soils and subtracting the mass washed off to calculate residual soil concentration. Ideally the mass washed off + the "wet" soil extraction should be equal to the amount of chemical originally on the "dry" soil. The percent recovery shows how close we actually came to that ideal value. The standard deviation in this section is the combined standard deviations of the terms that went into its calculation. In most cases the % recovery approaches 100% when one takes into account the standard deviation. This shows the reliability of the method was reasonable.

Table 5.1: PT#2 Summary of Chemical Masses

Average (of 3) Total Mass Washed off Soil after 5 Days (mg/g)

Vial	phenanthrene	phen SD	pyrene	pyr SD
A	0.0662	0.0032	0.0000	0.0000
B	0.0000	0.0000	0.0169	0.0008
AsBs	0.0341	0.0031	0.0147	0.0006
AB	0.0297	0.0021	0.0150	0.0098

Average (of 3) Mass Extracted From "Dry" Soil (mg/g)

Vial	phenanthrene	phen SD	pyrene	pyr SD
A	0.0782	0.0025	0.0000	0.0000
B	0.0000	0.0000	0.2157	0.0230
AsBs	0.0514	0.0094	0.0869	0.0023
AB	0.0400	0.0007	0.0883	0.0031

Average (of 3) Mass Extracted From "Wet" Soil (mg/g)

Vial	phenanthrene	phen SD	pyrene	pyr SD
A	0.0158	0.0140	0.0000	0.0000
B	0.0000	0.0000	0.1313	0.0091
AsBs	0.0000	0.0000	0.0592	0.0005
AB	0.0000	0.0000	0.0494	0.0018

Residual Soil Conc. (Initial mass - Mass washed off) (mg/g)

Vial	phenanthrene	phen SD	pyrene	pyr SD
A	0.0120	0.0057	0.0000	0.0000
B	0.0000	0.0000	0.1989	0.0238
AsBs	0.0173	0.0125	0.0722	0.0029
AB	0.0104	0.0028	0.0733	0.0128

(Mass Washed Off) + (Extracted From "Wet" Soil)

Vial	phenanthrene	phen SD	pyrene	pyr SD
A	0.0820	0.0172	0.0000	0.0000
B	0.0000	0.0000	0.1482	0.0100
AsBs	0.0341	0.0031	0.0739	0.0011
AB	0.0297	0.0021	0.0644	0.0116

% Recovery ((Washed off + "Wet")/"Dry")*100

Vial	phenanthrene	phen SD	pyrene	pyr SD
A	105	25	0	0
B	0	0	69	15
AsBs	66	24	85	4
AB	74	7	73	17

Table 5.2: PT#3 Summary of Chemical Masses

Average (of 3) Total Mass Washed off Soil after 5 Days (mg/g)

Vial	phenanthrene	phen SD	pyrene	pyr SD
A	0.1294	0.0045	0.0000	0.0000
B	0.0000	0.0000	0.0175	0.0007
AsBs	0.0759	0.0051	0.0157	0.0007
AB	0.0794	0.0014	0.0149	0.0011

Average (of 3) Mass Extracted From "Dry" Soil (mg/g)

Vial	phenanthrene	phen SD	pyrene	pyr SD
A	0.1493	0.0041	0.0000	0.0000
B	0.0000	0.0000	0.2157	0.0230
AsBs	0.0780	0.0027	0.0886	0.0064
AB	0.0830	0.0071	0.0758	0.0060

Average (of 3) Mass Extracted From "Wet" Soil (mg/g)

Vial	phenanthrene	phen SD	pyrene	pyr SD
A	0.0331	0.0028	0.0000	0.0000
B	0.0000	0.0000	0.1277	0.0030
AsBs	0.0141	0.0018	0.0491	0.0043
AB	0.0146	0.0016	0.0402	0.0023

Residual Soil Conc. (Initial Mass - Mass washed off) (mg/g)

Vial	phenanthrene	phen SD	pyrene	pyr SD
A	0.0199	0.0085	0.0000	0.0000
B	0.0000	0.0000	0.1982	0.0236
AsBs	0.0022	0.0079	0.0729	0.0071
AB	0.0035	0.0085	0.0609	0.0071

(Mass Washed Off) + (Extracted From "Wet" Soil)

Vial	phenanthrene	phen SD	pyrene	pyr SD
A	0.1625	0.0072	0.0000	0.0000
B	0.0000	0.0000	0.1452	0.0037
AsBs	0.0900	0.0069	0.0649	0.0050
AB	0.0941	0.0030	0.0551	0.0035

% Recovery ((Washed off + "Wet")/"Dry")*100

Vial	phenanthrene	phen SD	pyrene	pyr SD
A	109	8	0	0
B	0	0	67	12
AsBs	115	12	73	13
AB	113	12	73	12

Table 5.3: PT#4 Summary of Chemical Masses

Average (of 3) Total Mass Washed off Soil after 5 Days (mg/g)

Vial	phenanthrene	phen SD	pyrene	pyr SD
A	0.1732	0.0103	0.0000	0.0000
B	0.0000	0.0000	0.0191	0.0004
AsBs	0.1263	0.0050	0.0163	0.0004
AB	0.1227	0.0027	0.0162	0.0013

Average (of 3) Mass Extracted From "Dry" Soil (mg/g)

Vial	phenanthrene	phen SD	pyrene	pyr SD
A	0.3234	0.0100	0.0000	0.0000
B	0.0000	0.0000	0.2157	0.0230
AsBs	0.1423	0.0072	0.0811	0.0033
AB	0.1647	0.0134	0.0953	0.0070

Average (of 3) Mass Extracted From "Wet" Soil (mg/g)

Vial	phenanthrene	phen SD	pyrene	pyr SD
A	0.1506	0.0087	0.0000	0.0000
B	0.0000	0.0000	0.1165	0.0106
AsBs	0.0400	0.0048	0.0515	0.0035
AB	0.0273	0.0082	0.0446	0.0095

Residual Soil Conc. (Initial mass - Mass washed off) (mg/g)

Vial	phenanthrene	phen SD	pyrene	pyr SD
A	0.1502	0.0203	0.0000	0.0000
B	0.0000	0.0000	0.1966	0.0233
AsBs	0.0159	0.0122	0.0648	0.0037
AB	0.0420	0.0162	0.0791	0.0084

(Mass Washed Off) + (Extracted From "Wet" Soil)

Vial	phenanthrene	phen SD	pyrene	pyr SD
A	0.3238	0.0190	0.0000	0.0000
B	0.0000	0.0000	0.1356	0.0109
AsBs	0.1664	0.0098	0.0678	0.0040
AB	0.1499	0.0110	0.0608	0.0109

% Recovery ((Washed off + "Wet")/"Dry")*100

Vial	phenanthrene	phen SD	pyrene	pyr SD
A	100	9	0	0
B	0	0	63	16
AsBs	117	12	84	9
AB	91	15	64	19

PRACTICAL IMPLICATIONS

The findings that aqueous phase solubilities are dependent on soil phase concentrations have important practical implications. They are especially applicable for the design of pump and treat systems for cleaning subsurface environments in order to achieve low residual soil concentrations. Results with phenanthrene alone as well as with pyrene show that there is a dramatic decrease in water solubilities as soil concentrations decrease. Assuming similar effects will occur in the field, it can be concluded that the rate of cleanup will slow down dramatically as the clean up proceeds. To illustrate this trend, a series of pump and treat scenarios were calculated using the correlation developed in this study to show the volumes of water displacement needed to achieve progressively lower residual soil concentrations.

Plots were made showing the number of pore volumes that would be necessary to wash phenanthrene from the soil in all three situations (Phen A, Phen AsBs, Phen AB) given a specific target goal concentration (see Figures 5.26a,b,c). This was done by using a Microsoft Excel spreadsheet. A small program was written using the slopes that were obtained from the data to estimate the concentrations of the chemical in the pore water assuming that our definition of equilibrium was obtained in each case. At different soil concentrations, a different function would describe the water concentration for successive pore volume washings. An attempt was made to find a single equation that would describe the water concentration as a function of the soil concentration but we have so far been unsuccessful in our attempts.

In all three situations, complete elimination of the chemical from the soil was not possible due to the nature of the "Water Concentration Vs Soil Concentration" slopes at the lower levels. All three intercepted the x-axis (see Figures 5.13a, b, and c) and therefore this interception defined the limit of soil concentration attainable. The limits for each were as follows: Phen A = 6.165 mg/kg, Phen AsBs = 17.477 mg/kg, Phen AB = 10.259

mg/kg. Theoretically one would expect it to be possible for all of the chemical to be removed from the soil with enough pore volumes. Our data however did not support that notion.

A number of concepts should be considered when taking into account this apparent limit to chemical removal. After all, if there is indeed a limit to how much chemical can be removed from soil in this manner it would have far reaching implications, especially in terms of regulations driving such removal. First of all we must consider the fact that in all three of these cases there is no data for soil concentrations below about .01 mg/kg and therefore the function that was used to determine the water concentrations for soil concentrations lower than that was the same slope that was used to define the concentrations just above that. Therefore one might argue that the slope of the line may have changed at that point (become shallower) and therefore not crossed the x-axis as predicted.

One might also look at the plots and notice the very large error bars at the lower concentrations and argue that it is possible that the regression line should actually fall to the left of the one in place and therefore eliminate this limit idea or at least significantly lower it (see Figures 5.13a, b, and c). Although this is possible, it is not likely for a couple of reasons. First of all, in the case of the pure phenanthrene one can look at the overall chemical mass balance calculations (see Tables 5.1 - 5.3) and see that the calculated phenanthrene concentration which is plotted is actually lower than the concentration of phenanthrene that was extracted using hexane following the experiment (0.012 vs 0.0158 mg/g). This would indicate that the current regression line is actually to the left of where it should be based on possible error in initial sand estimations. This would result in a higher limit than is currently indicated. The initial sand concentration error only makes up part of the error bars however. The other part is due to the additive effect of all of the water concentration standard deviations that went into calculating the final sand concentration. In

this case for the error to result in a significant shift to the left of the current regression line it would mean that the water concentrations would have had to have been consistently estimated on the low side. There is no reason to believe that this is the case, especially since these estimations were done independently of each other on different days. It is more likely that the estimations alternate between high and low resulting in a negligible net effect.

One can see from all three plots (see Figures 5.25a,b,c) that as the limit in each case is approached, the amount of water necessary to wash off even a fraction of chemical grows exponentially. This would suggest that once a certain level of cleanup is obtained, it simply isn't practical to attempt to remove anymore chemical since it takes more and more water to remove less and less chemical. In reality the number of pore volumes necessary for this cleanup would likely be greater than what is estimated here because of our equilibrium assumption. The intention of these plots is to demonstrate the trend rather than to accurately indicate necessary pore volumes for actual cleanup.

A couple other interesting things to note is that we were working with a soil with essentially no organics present. This means that the chemical only had the surface of the soil and itself (or one other chemical in the case of the mixtures) to bind to. In the case of soils with high organic content, one could probably expect to see an even more pronounced increase in necessary pore volumes with additional removal.

Figure 5.26a: Pore Volumes Vs Treatment Goal (PhA)
(Initial Soil Concentration = 400 mg/kg Phenanthrene)

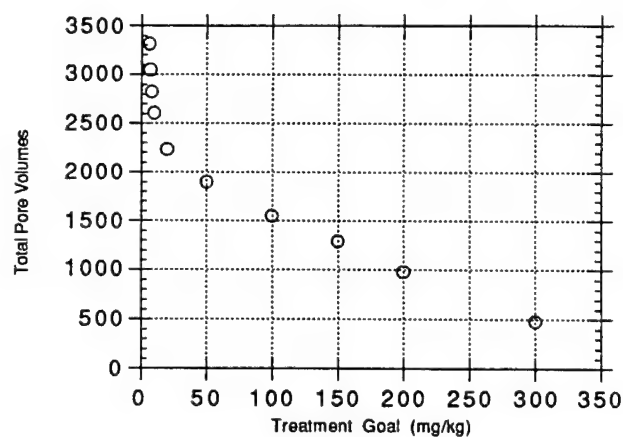


Figure 5.26b: Pore Volumes Vs Treatment Goal (Ph AsB₃)
(Initial Soil Conc = 400 mg/kg Phenanthrene)

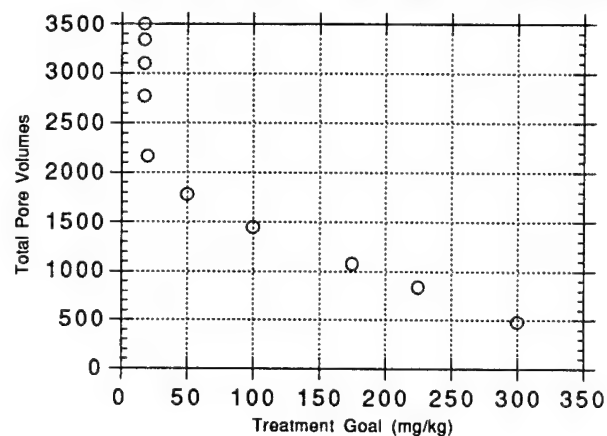
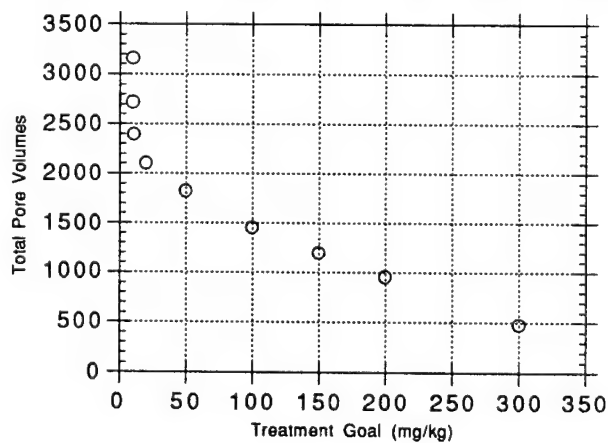


Figure 5.26c: Pore Volumes Vs Treatment Goal (PhAB)
(Initial Soil Concentration = 400 mg/kg Phenanthrene)



Chapter 6

CONCLUSIONS

CONCLUSIONS REGARDING ORIGINAL QUESTIONS

a) Is dissolution of a chemical from a soil dependent upon the amount of chemical remaining on the soil?

In this research, lower solubilities were obtained as phenanthrene soil concentrations decreased on low organic soil. In addition, there were strong linear correlations over narrow ranges of soil concentrations of about 0.1 mg/g or less for "Water Concentration Vs Soil Concentration" plots. It was found that regression slopes got progressively lower with increasing initial phenanthrene concentrations and therefore a nonlinear function is necessary to describe the trend over broad ranges of soil concentrations. An asymptotic increase in solution concentration was observed at higher soil concentrations implying that there is a soil concentration above which saturation concentrations can be expected of the solution in contact with it at equilibrium.

b) How does the presence of mixtures of chemicals affect their dissolution in comparison to pure compounds?

At low soil concentrations there is some evidence of a significant difference in dissolution between phenanthrene alone and phenanthrene present in a mixture with pyrene. At levels less than about 0.06 mg/g, phenanthrene seems to dissolve off less readily as a pure compound. However, at higher concentrations and over larger ranges of soil concentrations, this difference seems to become less significant.

c) Is there a difference between the dissolution of chemicals from soils coated with mixtures of chemicals and mixtures of soils each coated with individual chemicals?

Little difference was observed between the dissolution of chemicals from the soils with the two different mixture application methods at the soil concentrations that we worked with. The first method of application was the mixing of the soils themselves coated with the individual compounds and the second was the coating of soil with a mixture of the two compounds.

OTHER CONCLUSIONS

Low solution concentrations at low soil concentrations suggest that the bond holding molecules to the mineral surface is stronger than the bond holding the molecules to each other at higher soil concentrations.

Based on the comparison to a desorption isotherm with the same soil and chemical, the bond holding the molecules to the mineral surface in these experiments appears to be stronger than that of adsorption.

Based on the nonzero intercepts obtained in "Water Concentration Vs Soil Concentration" plots, there is some support that there are limits to how clean soil can get with mere water washing. Also, if our results were applied to pump and treat processes, we would expect to find a decrease in the amount of chemical removed with each additional pore volume wash.

The analysis of the results of this study provide a rational basis for predicting the amount of water necessary for reaching specified soil cleanup goals. Therefore such testing could play an important role in the designing of clean up methods.

Further studies with other chemicals should be carried out in order to shed additional light on this topic.

References

- Backhus, D.A., P.M. Gschwend and S. J. Eisenreich, 1995, "Sorption of Hydrophobic Organic Chemicals to Inorganic Surfaces: A Critical Review", *Environ. Sci. Technol.*, in review.
- Banerjee, S., 1984, "Solubility of Organic Mixtures in Water", *Environ. Sci. Technol.*, 18:587-591.
- Bewley, R., B. Ellis, P. Theile, I. Viney and J. Rees, 1989, "Microbial Clean-up of Contaminated Soil", *Chemistry & Industry (London)*, 778-783.
- Brusseau, M.L., 1991, "Cooperative Sorption of Organic Chemicals in Systems Composed of Low Organic Carbon Aquifer Materials", *Environ. Sci. Technol.*, 25:1747-1752.
- Chiou, P.V. and D.W. Schmedding, 1982, "Partitioning of Organic Compounds in Octanol-Water Systems", *Environ. Sci. Technol.*, 16:4-9.
- Eganhouse, R.P. and J.A. Calder, 1976, "The Solubility of Medium Molecular Weight Aromatic Hydrocarbons and the Effects of Hydrocarbon Co-Solutes and Salinity", *Geochimica et Cosmochimica Acta.*, 40:555-561.
- Feenstra, S., D.M. Mackay, and J.A. Cherry, 1991, "A Method for Assessing Residual NAPL Based on Organic Chemical Concentrations in Soil Samples", *Ground Water Monitoring Review*, 11:128-135.
- Fetter, C.W. 1993. *Contaminant Hydrogeology*. Macmillan Publishing Co, New York, NY.
- Jahan, K., 1993, Ph.D. thesis. "Biodegradation of Phenanthrene in Soils in the Presence of Surfactants". University of Minnesota.
- Karickhoff, S.W., D.S. Brown, and T.A. Scott, 1979, "Sorption of Hydrophobic Pollutants on Natural Sediments", *Water Research*, 13:241-248.
- Kiemele, M.J. and S.R. Schmidt. 1991. *Basic Statistics: Tools for Continuous Improvement*. Air Academy Press, Colorado Springs, CO.
- Lane, W.F. and R.C. Loehr, 1995, "Predicting Aqueous Concentrations of Polynuclear Aromatic Hydrocarbons in Complex Mixtures", *Water Environment Research*, 67:169-173.
- Lee, L.S., M. Hagwall, J.J. Delfino and P.S.C. Rao., 1992, "Partitioning of Polycyclic Aromatic Hydrocarbons from Diesel Fuel into Water", *Environ. Sci. Technol.*, 26:2104-2110.
- Lee, L.S., P.S.C. Rao and I. Okuda, 1992, "Equilibrium Partitioning of Polycyclic Aromatic Hydrocarbons from Coal Tar into Water", *Environ. Sci. Technol.*, 26:2110-2115.

- Liu, Z., S. Laha and R.G. Luthy, 1991, "Surfactant Solubilization of Polycyclic Aromatic Hydrocarbon Compounds in Soil-Water Suspensions", *Wat. Sci. Tech.*, 23:475-485.
- Mackay, D., W.Y. Shiu, and K.C. Ma, 1992. *Illustrated Handbook of Physical-Chemical Properties and Environmental Fate for Organic Chemicals Vol II*. Lewis Publishers, Chelsea, MI.
- Mader, B., 1994-95, Personal Communications.
- MacIntyre, W.G. and P.O. deFur, 1985, "The Effect of Hydrocarbon Mixtures on Adsorption of Substituted Naphthalenes by Clay and Sediment from Water", *Chemosphere*, 14:103-110.
- Maier, W.J., 1994-95, Personal Communications.
- Maier, W.J. et al. 1994 Final Report., "Bioremediation of Contaminated Soils - Aquifers on Reilly Site in St. Louis Park, Minnesota", University of Minnesota.
- Nelson, M.D., and W.J. Maier, 1995, "In Situ Bioremediation of Creosote Impacted Soil and Ground Water", *Proceedings 50th Purdue Industrial Waste Conference*, Purdue University, W. Lafayette, Indiana.
- Park, K.S., R.C. Sims and R.R. Dupont, 1990, "Transformation of PAHs in Soil Systems", *Journ. of Env. Eng.*, 116:632-640.
- Peters, C.A. and R.G. Luthy, 1993, "Coal Tar Dissolution in Water-Miscible Solvents: Experimental Evaluation", *Environ. Sci. Technol.*, 27:2831-2843.
- Schwarzenbach, R.P., P.M. Gschwend, and D.M. Imboden. 1993. *Environmental Organic Chemistry*. John Wiley & Sons, Inc., New York, NY.
- Smidt, D.P., 1995, M.S. thesis. "Sorption of Mixtures of Polycyclic Aromatic Hydrocarbons on Low Organic Content Soils". University of Minnesota.
- Sugatt, R.H., D.P. O'Grady, and S. Banerjee, 1984, "Toxicity of Organic Mixtures Saturated in Water to *Daphnia Magna*. Effect of Compositional Changes.", *Chemosphere.*, 13:11-18.
- Susurla, S., G.V. Bhoskar, and S.M. Rao Bhamidimarri, 1992, "Competitive Adsorption of Phenoxy Herbicide Chemical in Soil", *Wat. Sci. Tech.*, 26:2121-2124.
- Tam, E., 1994-95, Personal Communications.
- Verschuieren, Karel, 1983. *Handbook of Environmental Data on Organic Chemicals*. Van Nostrand Reinhold Company, New York, NY.
- Voice, T.C. and W.J. Weber Jr., 1983, "Sorption of Hydrophobic Compounds by Sediments, Soils and Suspended Solids - I", *Water Research*, 17:1433-1441.
- Weber, W.J., 1972. *Physicochemical Processes for Water Quality Control*. John Wiley & Sons, Inc., New York, NY.